


**Unity of Kohn-Sham density-functional theory and reduced-density-matrix-functional theory**Neil Qiang Su (苏乃强)<sup>✉\*</sup>*Department of Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education) and Renewable Energy Conversion and Storage Center (RECAST), Nankai University, Tianjin 300071, China* (Received 17 April 2021; revised 25 October 2021; accepted 26 October 2021; published 16 November 2021)

This work presents a rigorous theory to unify the two independent theoretical frameworks of Kohn-Sham (KS) density-functional theory (DFT) and reduced-density-matrix-functional theory (RDMFT). The generalization of the KS orbitals to hypercomplex number systems leads to the hypercomplex KS (HCKS) theory, which extends the search space for the electron density in KS-DFT and reformulates the kinetic energy. The HCKS theory provides a general framework, and different dimensions of the HCKS orbitals lead to different HCKS methods, with KS-DFT and RDMFT being two cases corresponding to the smallest and largest dimensions. Furthermore, a series of tests show that HCKS can capture the multireference nature of strong correlation by dynamically varying fractional occupations, while maintaining the same computational scaling as the KS method. With great potential to overcome the fundamental limitations of the KS method, HCKS creates new possibilities for the development and application of DFT.

DOI: [10.1103/PhysRevA.104.052809](https://doi.org/10.1103/PhysRevA.104.052809)**I. INTRODUCTION**

Built on the Hohenberg-Kohn theorem [1,2], Kohn-Sham (KS) density-functional theory (DFT) [3–5] is a formally exact theoretical framework toward the many-electron problem. Due to the favorable balance between accuracy and efficiency, KS-DFT has won enormous popularity that can manifest itself in the countless applications across physics, materials science, chemistry, and biology [6–8]. Nonetheless, the great success of KS-DFT, along with commonly used density-functional approximations (DFAs), is clouded by the improper treatment of strong correlation [9]. Strong correlation represents the intractable electronic interaction stemming from the multireference character of systems, which has long posed a major challenge to KS-DFT [10–14].

It is generally recognized that intrinsic errors in commonly used DFAs [9,15–21] and the slow progress in systematically eliminating these errors for better describing strong correlation have severely limited the applicability of KS-DFT [9,19,22,23]. The enlightening work by Lee, Bertels, Small, and Head-Gordon [24] shows that commonly used DFAs can better treat the strong correlation in singlet biradicals by using complex spin-restricted orbitals in KS-DFT. This thus raises a deep question: In addition to the errors inherent in existing DFAs, is there still any limitation in the understanding and application of the KS-DFT framework? Apparently, in-depth insights into this question is important for further development and application of DFT.

Besides KS-DFT, reduced-density-matrix-functional theory (RDMFT) [25–33] provides an alternative approach to the many-electron problem. The Gilbert's theorem [25] guarantees that the one-electron reduced-density matrix (1-RDM)

instead of the density can be used as the fundamental variable for the energy functional, which thus makes RDMFT an exact theoretical framework independent of KS-DFT. RDMFT has proved its great potential to overcome the fundamental limitations of KS-DFT through the successful application in predicting dissociation energy curves [34–36], and fundamental gaps for finite systems and extended solids [37] as well as for Mott insulators [29]. Therefore, establishing a connection with the theoretical framework of RDMFT will further improve our understanding of KS-DFT and the problems of existing DFAs.

This work presents theory to unify the two theoretical frameworks of KS-DFT and RDMFT. This is achieved by generalizing the conventional KS determinant to hypercomplex number systems. The resulting hypercomplex KS (HCKS) theory extends the search space for the electron density in KS-DFT and reformulates the kinetic energy in a form similar to that in RDMFT. The potential of HCKS in capturing the physical essence of strong correlation is demonstrated on systems of multireference character, including transition metals.

The rest of this article is structured as follows. First, KS-DFT and RDMFT are reviewed and their differences are summarized in Sec. II and Sec. III. After that, the HCKS theory is introduced in Sec. IV, which is proved to unify the two theoretical frameworks of KS-DFT and RDMFT. Finally, the numerical test results of HCKS are discussed in Sec. V, followed by conclusions in Sec. VI.

**II. KOHN-SHAM DENSITY-FUNCTIONAL THEORY**

KS-DFT introduces a noninteracting system, namely the KS system, which yields the same electron density as the interacting system [3,4]. Based on this, the total energy as a

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function of the electron density can be expressed as

$$E_{\text{tot}}[\rho_\sigma] = T_s[\rho_\sigma] + E_{\text{ext}}[\rho_\sigma] + E_{\text{H}}[\rho_\sigma] + E_{\text{XC}}[\rho_\sigma], \quad (1)$$

which includes the kinetic energy of the KS system  $T_s[\rho_\sigma]$ , the external energy  $E_{\text{ext}}[\rho_\sigma]$ , the Coulomb energy  $E_{\text{H}}[\rho_\sigma]$ , and the exchange-correlation (XC) energy  $E_{\text{XC}}[\rho_\sigma]$ . Here  $\sigma$  denote the electron spin, which can be spin-up ( $\alpha$ ) and -down ( $\beta$ ).

The ground-state wave function of the KS system is just a determinant that is constructed by the occupied KS orbitals,

$$\Phi = \begin{vmatrix} \varphi_1^\alpha(\mathbf{r}_1)\alpha & \varphi_2^\alpha(\mathbf{r}_1)\alpha & \cdots & \varphi_1^\beta(\mathbf{r}_1)\beta & \varphi_2^\beta(\mathbf{r}_1)\beta & \cdots \\ \varphi_1^\alpha(\mathbf{r}_2)\alpha & \varphi_2^\alpha(\mathbf{r}_2)\alpha & \cdots & \varphi_1^\beta(\mathbf{r}_2)\beta & \varphi_2^\beta(\mathbf{r}_2)\beta & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \varphi_1^\alpha(\mathbf{r}_N)\alpha & \varphi_2^\alpha(\mathbf{r}_N)\alpha & \cdots & \varphi_1^\beta(\mathbf{r}_N)\beta & \varphi_2^\beta(\mathbf{r}_N)\beta & \cdots \end{vmatrix}. \quad (2)$$

This determinant, termed the KS determinant, makes it viable to express the electron density in the simple form,

$$\rho_\sigma(\mathbf{r}) = \sum_{k=1}^{N_\sigma} |\varphi_k^\sigma(\mathbf{r})|^2. \quad (3)$$

With Eq. (2), the kinetic energy  $T_s[\rho_\sigma]$  can be obtained via

$$T_s[\rho_\sigma] = \langle \Phi | \hat{T} | \Phi \rangle = -\frac{1}{2} \sum_{\sigma} \sum_{k=1}^{N_\sigma} \langle \varphi_k^\sigma | \nabla^2 | \varphi_k^\sigma \rangle, \quad (4)$$

and the XC energy is defined by

$$E_{\text{XC}}[\rho_\sigma] = T[\rho_\sigma] - T_s[\rho_\sigma] + E_{\text{ee}}[\rho_\sigma] - E_{\text{H}}[\rho_\sigma], \quad (5)$$

where  $T[\rho_\sigma]$  and  $E_{\text{ee}}[\rho_\sigma]$  are the kinetic energy and the electron-electron interacting energy of the interacting physical system, respectively. Hence the XC energy includes contributions from both the kinetic energy (i.e.,  $T[\rho_\sigma] - T_s[\rho_\sigma]$ ) and the electron-electron interacting energy (i.e.,  $E_{\text{ee}}[\rho_\sigma] - E_{\text{H}}[\rho_\sigma]$ ).

Among the four terms in Eq. (1), the density functionals of  $E_{\text{ext}}[\rho_\sigma]$  and  $E_{\text{H}}[\rho_\sigma]$  are well defined [38], and  $T_s[\rho_\sigma]$  can be calculated via Eq. (4); only the exact functional of  $E_{\text{XC}}[\rho_\sigma]$  is unknown, which has to be obtained by approximation in practice. To date, there are various DFAs for  $E_{\text{XC}}[\rho_\sigma]$  constructed from different philosophies and strategies [3,39–56].

The ground-state energy in KS-DFT can be obtained by the minimization of  $E_{\text{tot}}[\rho_\sigma]$  with respect to  $\{\varphi_p^\sigma\}$ , subject to the orthonormalization condition

$$\langle \varphi_p^\sigma | \varphi_q^\sigma \rangle = \delta_{pq}. \quad (6)$$

This process can be easily carried out through the self-consistent field (SCF) calculation of the KS equations [3].

### III. REDUCED DENSITY MATRIX FUNCTIONAL THEORY

In RDMFT, the total energy [2,25] is

$$E_{\text{tot}}[\gamma_\sigma] = T[\gamma_\sigma] + E_{\text{ext}}[\gamma_\sigma] + E_{\text{H}}[\gamma_\sigma] + E_{\text{XC}}[\gamma_\sigma], \quad (7)$$

where  $T[\gamma_\sigma]$ ,  $E_{\text{ext}}[\gamma_\sigma]$ ,  $E_{\text{H}}[\gamma_\sigma]$ , and  $E_{\text{XC}}[\gamma_\sigma]$  are now uniquely determined by 1-RDM ( $\gamma_\sigma$ ). Unlike KS-DFT, there is no noninteracting counterpart to the physical system in RDMFT, hence  $\gamma_\sigma$  should be obtained from the wave function of the interacting system, instead of from a simple wave function

similar to Eq. (2). This thus makes the RDMFT calculation much more complicated as compared to KS-DFT.

The diagonalization of  $\gamma_\sigma$  leads to the natural spin orbitals  $\{\psi_p^\sigma\}$  and their occupations  $\{n_p^\sigma\}$ , which in turn form the spectral representation of  $\gamma_\sigma$ ,

$$\gamma_\sigma = \sum_{p=1}^K |\psi_p^\sigma\rangle n_p^\sigma \langle \psi_p^\sigma|, \quad (8)$$

where  $K$  is the dimension of the basis set. With Eq. (8),  $E_{\text{H}}[\gamma_\sigma]$  and any (non-)local  $E_{\text{ext}}[\gamma_\sigma]$  can be expressed in terms of  $\{\psi_p^\sigma\}$  and  $\{n_p^\sigma\}$  [38], and  $T[\gamma_\sigma]$  takes the following form:

$$T[\gamma_\sigma] = -\frac{1}{2} \sum_{\sigma} \sum_{p=1}^K n_p^\sigma \langle \psi_p^\sigma | \nabla^2 | \psi_p^\sigma \rangle. \quad (9)$$

Unlike KS-DFT,  $T[\gamma_\sigma]$  in RDMFT can exactly take into account the kinetic energy of the interacting physical system, and the XC energy in RDMFT is completely from the electron-electron interaction,

$$E_{\text{XC}}[\gamma_\sigma] = E_{\text{ee}}[\gamma_\sigma] - E_{\text{H}}[\gamma_\sigma], \quad (10)$$

which needs to be obtained by approximation in practice. Different approximations for  $E_{\text{XC}}[\gamma_\sigma]$  have been proposed during the past few decades, some are explicit functionals of  $\gamma_\sigma$ , while most depend on  $\gamma_\sigma$  implicitly through  $\{\psi_p^\sigma\}$  and  $\{n_p^\sigma\}$  [26,27,29,30,34,35,57–60]. Nonetheless, existing 1-RDM functionals in RDMFT still show large errors in the description of various properties that can be properly predicted by KS-DFT, which should be attributed to the incorrect weak-correlation limits [61] and the incorrect description of spin-polarized systems [62] of the functionals, as well as the underestimated dynamic correlation by most existing functionals that depend only on the Coulomb and exchange integrals [63,64].

The ground-state energy in RDMFT is obtained by the minimization of  $E_{\text{tot}}[\gamma_\sigma]$  with respect to  $\gamma_\sigma$  or, equivalently, with respect to both  $\{\psi_p^\sigma\}$  and  $\{n_p^\sigma\}$ , subject to the orthonormalization constraint on  $\{\psi_p^\sigma\}$ ,

$$\langle \psi_p^\sigma | \psi_q^\sigma \rangle = \delta_{pq}, \quad (11)$$

and the ensemble  $N$ -representability constraint on  $\{n_p^\sigma\}$  [65,66],

$$0 \leq n_p^\sigma \leq 1, \quad \sum_{p=1}^K n_p^\sigma = N_\sigma. \quad (12)$$

In addition, the density in RDMFT can be obtained from the diagonal element  $\langle \mathbf{r} | \gamma_\sigma | \mathbf{r} \rangle$ ,

$$\rho_\sigma(\mathbf{r}) = \sum_{p=1}^K n_p^\sigma |\psi_p^\sigma(\mathbf{r})|^2. \quad (13)$$

Compared with Eq. (3), the density in Eq. (13) has a wider search space, and the fractional occupations can capture the multireference character of the system under study. Therefore, despite the computational disadvantage, RDMFT has the potential to overcome the fundamental limitations of KS-DFT, especially in the description of strong correlation.

#### IV. HYPERCOMPLEX KOHN-SHAM THEORY

Obviously, the density of Eq. (3) that corresponds to a single determinant cannot effectively capture the multireference character of the system under study, which thus makes it extremely difficult to solve the strong correlation problem within the conventional KS-DFT framework. Unlike many attempts made to combine DFT with multiconfiguration states, here we present a different idea to address the strong correlation issue in KS-DFT by generalizing the KS orbitals and the KS determinant to hypercomplex number systems. Next, the HCKS theory that unifies KS-DFT and RDMFT will be introduced, more detailed derivation can be found in the Supplemental Material [38].

##### A. Energy and one-electron equations in HCKS

The concept of hypercomplex and the theory of Clifford algebra [38,67] that generalizes the real and complex numbers to quaternions, octonions, and other hypercomplex numbers have important applications in a variety of fields including theoretical physics [68]. Based on these, the KS orbitals are generalized to hypercomplex number systems, which take the following form:

$$\varphi_p^\sigma(\mathbf{r}) = \phi_p^{\sigma,0}(\mathbf{r}) + \sum_{\mu=1}^n \phi_p^{\sigma,\mu}(\mathbf{r})e_\mu, \quad (14)$$

where  $\{\phi_p^{\sigma,\mu}\}$  are a set of real functions, and  $\{e_1, e_2, \dots, e_n\}$  are a basis of dimension  $n$  in a Clifford algebra, such that [68]

$$e_\mu^2 = -1; e_\mu e_\nu = -e_\nu e_\mu. \quad (15)$$

The orbitals defined by Eq. (14) are called the HCKS orbitals, and the determinant formed by them is called the HCKS determinant  $\Phi^{\text{HC}}$ . The HCKS orbitals are actually a set of high-dimensional KS orbitals, while the real and complex KS orbitals in the conventional KS method are the special cases for  $n = 0$  and  $n = 1$ , respectively. Moreover, the conjugate hypercomplex [38,68] of the HCKS orbitals read

$$\bar{\varphi}_p^\sigma(\mathbf{r}) = \phi_p^{\sigma,0}(\mathbf{r}) - \sum_{\mu=1}^n \phi_p^{\sigma,\mu}(\mathbf{r})e_\mu. \quad (16)$$

In HCKS, the auxiliary system taking the HCKS determinant  $\Phi^{\text{HC}}$  as the ground state is used as the noninteracting system subject to the external potential  $\hat{V}_s^\sigma = \sum_i^{N_\sigma} v_s^\sigma(\mathbf{r}_i)$ . Hence the ground-state energy of the noninteracting system is

$$\begin{aligned} E_s^{\text{HC}}[\rho_\sigma] &= \langle \Phi^{\text{HC}} | \hat{T} + \hat{V}_s | \Phi^{\text{HC}} \rangle \\ &= T_s^{\text{HC}}[\rho_\sigma] + \sum_\sigma \int v_s^\sigma(\mathbf{r})\rho_\sigma(\mathbf{r})d\mathbf{r}, \end{aligned} \quad (17)$$

where the density  $\rho_\sigma$  and the kinetic energy  $T_s^{\text{HC}}[\rho_\sigma]$  can be obtained by inserting the HCKS orbitals into Eqs. (3) and (4), respectively, while the potential  $\hat{V}_s^\sigma$  is chosen to make the noninteracting system yield the same density as the interacting physical system. Following the variational principle based on the HCKS orbitals subject to the orthonormalization condition, a set of one-electron eigenvalue equations can be

derived, which are

$$\hat{h}^\sigma \varphi_p^\sigma(\mathbf{r}) = \varepsilon_p^\sigma \varphi_p^\sigma(\mathbf{r}), \quad (18)$$

where the operator  $\hat{h}^\sigma$  is

$$\hat{h}^\sigma = -\frac{1}{2}\nabla^2 + v_s^\sigma(\mathbf{r}). \quad (19)$$

Making use of Eq. (14), Eq. (18) can be further expanded as

$$\begin{aligned} \hat{h}^\sigma \phi_p^{\sigma,0}(\mathbf{r}) &= \varepsilon_p^\sigma \phi_p^{\sigma,0}(\mathbf{r}) \\ \hat{h}^\sigma \phi_p^{\sigma,1}(\mathbf{r}) &= \varepsilon_p^\sigma \phi_p^{\sigma,1}(\mathbf{r}) \\ &\dots \\ \hat{h}^\sigma \phi_p^{\sigma,n}(\mathbf{r}) &= \varepsilon_p^\sigma \phi_p^{\sigma,n}(\mathbf{r}). \end{aligned} \quad (20)$$

Hence, Eq. (18) are a set of high-dimensional KS equations, named the HCKS equations.

The solution of the HCKS equations yields the exact density, and the ground-state energy of the interacting system can be obtained via

$$E_{\text{tot}}[\rho_\sigma] = T_s^{\text{HC}}[\rho_\sigma] + E_{\text{ext}}[\rho_\sigma] + E_{\text{H}}[\rho_\sigma] + E_{\text{XC}}^{\text{HC}}[\rho_\sigma]. \quad (21)$$

The generalization of the KS orbitals and determinant to hypercomplex number systems makes  $T_s^{\text{HC}}[\rho_\sigma]$  different from  $T_s[\rho_\sigma]$  in KS; accordingly, the XC energy in HCKS should be defined as

$$E_{\text{XC}}^{\text{HC}}[\rho_\sigma] = T[\rho_\sigma] - T_s^{\text{HC}}[\rho_\sigma] + E_{\text{ee}}[\rho_\sigma] - E_{\text{H}}[\rho_\sigma], \quad (22)$$

where the contribution from the kinetic energy is different from that of KS, while the contribution from the electron-electron interaction remains unchanged. Here the superscript HC is used to distinguish from the definitions in KS.

To realize this HCKS approach, the potential  $v_s^\sigma$  in Eq. (19) needs to be clearly defined. From the stationary property, the total energies of both the noninteracting and the interacting systems, i.e., Eqs. (17) and (21), must be invariant under small changes  $\delta\rho_\sigma$  around the exact density  $\rho_\sigma$ , subject to the condition  $\int \delta\rho_\sigma(\mathbf{r})d\mathbf{r} = 0$ . With these,  $v_s^\sigma$  can be determined up to within a constant, that is,

$$v_s^\sigma(\mathbf{r}) = v_{\text{H}}(\mathbf{r}) + v_{\text{XC}}^{\text{HC}\sigma}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}), \quad (23)$$

where  $v_{\text{ext}}(\mathbf{r})$  is the external potential and  $v_{\text{H}}(\mathbf{r})$  and  $v_{\text{XC}}^{\text{HC}\sigma}(\mathbf{r})$  are the Coulomb and XC potentials, which are obtained via the functional derivatives  $\frac{\delta E_{\text{H}}[\rho_\sigma]}{\delta\rho_\sigma(\mathbf{r})}$  and  $\frac{\delta E_{\text{XC}}^{\text{HC}}[\rho_\sigma]}{\delta\rho_\sigma(\mathbf{r})}$ , respectively. Due to the dependence of this potential on the density, the HCKS equations need to be solved self-consistently.

The above discussion shows that the HCKS theory is exact, except that the unknown XC functional needs to be obtained by approximation in practice. Moreover, HCKS as well as KS is based on a pure state, and thus it can circumvent the generalized Pauli constraints that hamper RDMFT [69]. Note that Eqs. (18) and (20) are not the equations to be solved in practical applications. Next, the further derivations on the density and kinetic energy will result in a set of easy-to-solve auxiliary equations for the HCKS calculation.

### B. Density and kinetic energy in HCKS

Without loss of generality,  $\{\phi_p^{\sigma,\mu}\}$  in Eq. (14) can be expanded on a set of orthonormal functions  $\{\xi_p\}$

$$\phi_p^{\sigma,\mu}(\mathbf{r}) = \sum_{q=1}^K \xi_q(\mathbf{r}) V_{pq}^{\sigma,\mu}. \quad (24)$$

Here  $V^{\sigma,\mu}$  is a  $K \times K$  matrix associated with the  $\mu$ th component of the HCKS orbitals for each  $\mu$  in  $[0, n]$ . Making use of Eq. (24), the orthonormalization condition of Eq. (6) becomes (see the Supplemental Material [38])

$$\sum_{\mu=0}^n V^{\sigma,\mu} V^{\sigma,\mu T} = \sum_{\mu=0}^n V^{\sigma,\mu T} V^{\sigma,\mu} = I_K, \quad (25)$$

and

$$\begin{aligned} V^{\sigma,\mu} V^{\sigma,\nu T} &= V^{\sigma,\nu} V^{\sigma,\mu T}; \\ V^{\sigma,\mu T} V^{\sigma,\nu} &= V^{\sigma,\nu T} V^{\sigma,\mu}, \end{aligned} \quad (26)$$

where the superscript  $T$  denotes the transpose and  $I_K$  is the  $K \times K$  identity matrix. Inserting Eqs. (14) and (24) into Eq. (3) leads to the electron density corresponding to the HCKS determinant,

$$\rho_\sigma(\mathbf{r}) = \sum_{p,q=1}^K \xi_p(\mathbf{r}) D_{pq}^\sigma \xi_q(\mathbf{r}), \quad (27)$$

where  $D^\sigma$  is a symmetric matrix,

$$D^\sigma = \sum_{\mu=0}^n V^{\sigma,\mu T} I_K^{N_\sigma} V^{\sigma,\mu}, \quad (28)$$

and  $I_K^{N_\sigma}$  is a  $K \times K$  diagonal matrix, with the first  $N_\sigma$  diagonal elements being 1 and the rest being 0. The diagonalization of  $D^\sigma$  leads to

$$D^\sigma = U^\sigma \Lambda^\sigma U^{\sigma T}, \quad (29)$$

where  $U^\sigma$  is an orthogonal matrix and  $\Lambda^\sigma$  is a diagonal matrix with the diagonal elements being the eigenvalues of  $D^\sigma$  and satisfying the following constraints (see the Supplemental Material [38]):

$$0 \leq \lambda_p^\sigma \leq 1; \quad \sum_{p=1}^K \lambda_p^\sigma = N_\sigma. \quad (30)$$

With Eq. (29), the density of Eq. (27) can be further formulated as

$$\rho_\sigma(\mathbf{r}) = \sum_{p=1}^K \lambda_p^\sigma |\chi_p^\sigma(\mathbf{r})|^2, \quad (31)$$

where  $\{\chi_p^\sigma\}$  are obtained from the unitary transformation,  $\chi_p^\sigma(\mathbf{r}) = \sum_{q=1}^K \xi_q(\mathbf{r}) U_{qp}^\sigma$ , and hence they are orthonormal,

$$\langle \chi_p^\sigma | \chi_q^\sigma \rangle = \delta_{pq}. \quad (32)$$

Through a series of similar derivations, the kinetic energy corresponding to the HCKS determinant can be

formulated as

$$T_s[\rho_\sigma] = -\frac{1}{2} \sum_{\sigma} \sum_{p=1}^K \lambda_p^\sigma \langle \chi_p^\sigma | \nabla^2 | \chi_p^\sigma \rangle. \quad (33)$$

Therefore, although the HCKS orbitals and determinant are hypercomplex, the electron density and kinetic energy are both real. The above derivations show that the introduction of the HCKS orbitals generalizes the electron density and the kinetic energy in KS, i.e., Eqs. (3) and (4), to Eq. (31) and Eq. (33) that have the similar forms as the electron density and kinetic energy in RDMFT. Moreover, the additional constraints, i.e., Eq. (30) on  $\{\lambda_p^\sigma\}$  and Eq. (32) on  $\{\chi_p^\sigma\}$ , are the same to the constraints on natural spin orbitals and their occupations as well. The number of orbitals in  $\{\chi_p^\sigma\}$  that are allowed for fractional occupations relates to the dimension of the HCKS orbitals (i.e.,  $n+1$ ). KS is the case of  $n=0$ , which has all  $\{\chi_p^\sigma\}$  integer occupied; while the recently developed complex spin-restricted KS (cRKS) [24] corresponds to the case of  $n=1$ , where two of  $\{\chi_p^\sigma\}$  can be half filled for singlet biradicals. For completeness, next it will be further proved that when the dimension of the HCKS orbitals is greater than or equal to the dimension of the basis set, i.e.,  $n+1 \geq K$ , there is no additional constraint on  $\{\chi_p^\sigma\}$  and  $\{\lambda_p^\sigma\}$  other than Eqs. (30) and (32).

Here provide a proof by contradiction, and assume that there are more constraints on  $\{\chi_p^\sigma\}$  or  $\{\lambda_p^\sigma\}$  besides Eqs. (30) and (32) when  $n+1 \geq K$ . In order to prove this assumption is wrong, we only need to find a special example that there is no other constraint on  $\{\chi_p^\sigma\}$  or  $\{\lambda_p^\sigma\}$  besides Eqs. (30) and (32) when  $n+1 = K$ . If so, then the cases of  $n+1 > K$  certainly will bring no additional constraint either, since it has greater degrees of freedom with larger  $n$ . To achieve this end, a special set of HCKS orbitals for  $n+1 = K$  are considered below.

Given any set of orthonormal  $\{\chi_p^\sigma\}$ , the HCKS orbitals can be constructed by taking the following simple form for  $\{\phi_p^{\sigma,\mu}\}$  in Eq. (14),

$$\phi_p^{\sigma,\mu} = \chi_{\mu+1}^\sigma(\mathbf{r}) V_{p\mu+1}^{\sigma,\mu}. \quad (34)$$

It means that the components corresponding to the same  $e_\mu$  in all the HCKS orbitals are formed by the same function  $\chi_{\mu+1}^\sigma$ , thereby

$$V_{pq}^{\sigma,\mu} = \begin{cases} W_{pq}^\sigma, & q = \mu + 1 \\ 0, & q \neq \mu + 1, \end{cases} \quad (35)$$

where  $W^\sigma$  is a  $K \times K$  matrix. By inserting Eq. (35) into Eqs. (25) and (26), the orthonormalization condition becomes (see the Supplemental Material [38])

$$W^\sigma W^{\sigma T} = I_K, \quad (36)$$

which thus requires  $W^\sigma$  to be an orthogonal matrix. With the definition of  $V^{\sigma,\mu}$  by Eq. (35), the same derivations as above can lead to Eqs. (31) and (33) for  $\rho_\sigma(\mathbf{r})$  and  $T[\rho_\sigma]$  as well, while  $\lambda_p^\sigma = \sum_{k=1}^{N_\sigma} (W_{kp}^\sigma)^2$ . As  $W^\sigma$  can be any orthogonal matrix,  $\{\lambda_p^\sigma\}$  can take any values subject to Eq. (30). This conclusion contradicts the above assumption, which thus verifies that Eqs. (30) and (32) are the only constraints on  $\{\chi_p^\sigma\}$  and  $\{\lambda_p^\sigma\}$  when  $n+1 \geq K$ .

Overall, the introduction of the HCKS orbitals leads to a set of auxiliary orbitals  $\{\chi_p^\sigma\}$  and their occupations  $\{\lambda_p^\sigma\}$ ,



which extends the search space for the electron density and formulates the kinetic energy with  $\{\chi_p^\sigma\}$  and  $\{\lambda_p^\sigma\}$ . In theory,  $\{\chi_p^\sigma\}$  and  $\{\lambda_p^\sigma\}$  take the electron density as the basic variable, which thus provide more flexibility in constructing approximate functionals toward better consideration of the XC effect in HCKS. The dimension of the HCKS orbitals (i.e.,  $n + 1$ ) determines the degree of restriction on  $\{\lambda_p^\sigma\}$ , which achieves correspondingly different HCKS methods. When  $n$  takes the minimum value, that is,  $n = 0$ ,  $\{\lambda_p^\sigma\}$  are subject to the strongest restriction and can only be integer, thus HCKS reduces to KS; when  $n > 0$ ,  $\{\lambda_p^\sigma\}$  can be fractional, subject to the constraint of Eq. (30). More constraints on  $\{\lambda_p^\sigma\}$  need to be further explored for different  $n$  except  $n + 1 \geq K$ . It has been proved above that when  $n + 1 \geq K$ , Eqs. (32) and (30) are the only constraints on  $\{\chi_p^\sigma\}$  and  $\{\lambda_p^\sigma\}$ , respectively, which are actually equivalent to the constraints on natural spin orbitals and their occupations, that is, Eqs. (11) and (12) in RDMFT. Moreover, the kinetic energy, the external energy, and the Coulomb energy in HCKS have the same forms as those in RDMFT, and in the construction of the XC functional,  $\{\chi_p^\sigma\}$  and  $\{\lambda_p^\sigma\}$  for  $n + 1 \geq K$  provide the equivalent information as the natural spin orbitals and their occupations. Consequently, the ground-state energy in HCKS (in the case of  $n + 1 \geq K$ ) obtained via the minimization of the energy functional with respect to both  $\{\chi_p^\sigma\}$  and  $\{\lambda_p^\sigma\}$  equates with the ground-state energy in RDMFT obtained via the minimization of the energy functional with respect to both natural spin orbitals and their occupations. Therefore, RDMFT is a special case of the newly developed HCKS theory, which provides a general theoretical framework to unify KS-DFT and RDMFT.

### C. Auxiliary working equations in HCKS

So far, the HCKS theory has been constructed. In practice, the ground-state energy in HCKS is obtained by the minimization of the total energy with respect to both  $\{\chi_p^\sigma\}$  and  $\{\lambda_p^\sigma\}$ . Unlike RDMFT, the costly minimization with respect to  $\{\chi_p^\sigma\}$  in HCKS can be achieved via the following equations:

$$\hat{h}^\sigma \chi_p^\sigma(\mathbf{r}) = \bar{\epsilon}_p^\sigma \chi_p^\sigma(\mathbf{r}). \quad (37)$$

Here the density required in  $\hat{h}^\sigma$  is constructed by Eq. (31), and hence Eq. (37) can be solved through a simple SCF calculation similar to that of KS-DFT. Therefore, HCKS has the same computational scaling as KS-DFT. Note that for complicated functionals that depend on  $\{\chi_p^\sigma\}$  and  $\{\lambda_p^\sigma\}$ , the chain rule should be applied to derive  $\hat{h}^\sigma$ , or gradient-based algorithms should be used for the HCKS calculation.

## V. RESULTS

The numerical performance of HCKS and its potential in describing strong correlation are evaluated with the finite basis simulation. All calculations were performed using a local modified version of the NWChem package [70], and the HCKS method with  $n + 1 = K$  is tested in this work. Systems of multireference character are calculated, including C atom under varying external charged environments, various atoms and diatoms from the TS12 benchmark set [71], atoms of transition metals, and the C<sub>2</sub> molecule with stretched bond. The basis sets used are aug-cc-pVQZ [72,73] for main-group

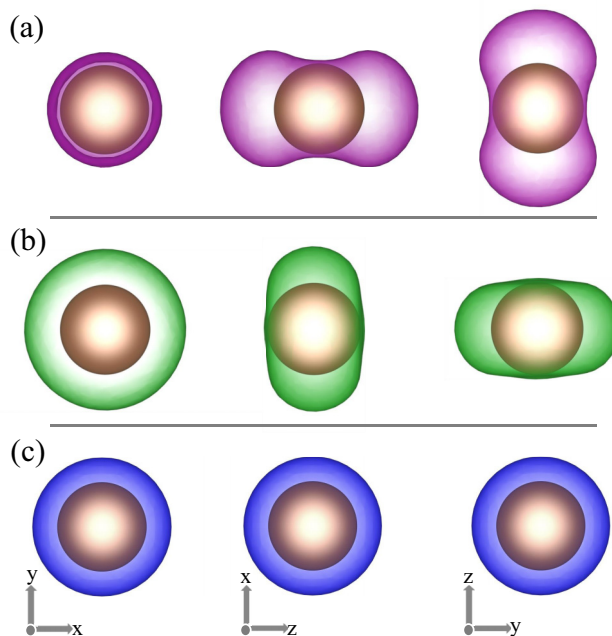


FIG. 1. Density on real-space grids for the lowest singlet state of C atom. (a) RKS density (purple), (b) cRKS density (green), and (c) HCKS density (blue) are plotted at the isosurface value of 0.2 au. Views along the  $z$ ,  $y$ , and  $x$  axes are provided respectively. The PBE XC functional is applied for all the calculation.

elements, and def2-TZVP [74] for transition-metal elements. In principle, HCKS and KS have different definitions of XC functionals. Nevertheless, the XC functionals that are commonly used in KS, namely PBE [45] and BLYP [42,43], are used in both HCKS and KS for most tests in this work, which can directly and effectively compare the differences between the two theoretical frameworks. Moreover, the use of functionals that have been proved effective in KS can make HCKS have the good merits of KS, as HCKS would reduce to KS when the strong correlation effect is not obvious. In the future, functionals developed specifically for HCKS can further improve the performance of HCKS. A distinct advantage of the HCKS and KS calculations in this work is that the results converge fast with respect to the size of the basis set, while the calculations of RDMFT with common 1-RDM functionals suffer from the same issue of slow convergence [75,76] as the wave-function methods [77], which has recently been attributed to the off-diagonal cusp in 1-RDM [78]. A numerical test on the basis set dependence of HCKS, KS, and RDMFT can be found in Fig. S1 of the Supplemental Material [38].

The density for the lowest singlet state of C atom is first examined. The singlet-state C atom is of biradical nature, with two electrons in the  $2p$  subshell. Normally, the spin-restricted KS (RKS) would have one doubly occupied  $p$  orbital and destroy the degeneracy of the  $p$  orbitals. Figure 1(a) shows the density of RKS when  $p_z$  is occupied, which maintains the spin symmetry but loses the space symmetry. Different from RKS, cRKS leads to two half-filled  $p$  orbitals for the singlet C atom [24]; see the Supplemental Material [38]. Figure 1(b) shows that the cRKS density with both  $p_x$  and  $p_y$  half filled maintains

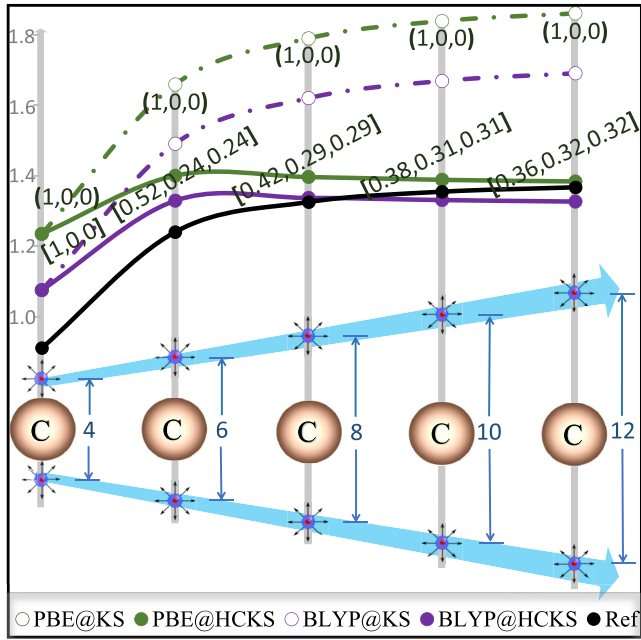


FIG. 2. Triplet-singlet energy gaps of C atom under varying external charged environments. The energies are calculated with two point charges of 0.3 au placed equidistantly on two sides of the C atom, with the distance between the two point charges ranging from 4 to 12 Å. KS and HCKS in use of the same XC functionals (PBE and BLYP) are examined, while CCSDT [79] results are used as reference. For both KS and HCKS, spin-restricted and spin-unrestricted calculations are performed for singlet and triplet states, respectively. All energies are in eV. The occupations of the three  $p$  orbitals for the singlet states are also provided in the figure, and the occupations by KS and HCKS (in use of PBE functional) are in round and square brackets, respectively. By comparison, the occupations by KS keep unchanged, while HCKS can provide dynamically varying fractional occupations under different charged environments.

the space symmetry along the  $z$  axis, but it cannot guarantee the space symmetry along both the  $x$  and  $y$  axes. In contrast, the spin-restricted solution of HCKS provides three equally occupied  $p$  orbitals, each  $p$  orbital is  $1/3$  filled. Therefore, the density by HCKS can maintain both spin and space symmetry; see Fig. 1(c). Similar results can be obtained for other systems of multireference character such as singlet states of O, S, and Si atoms, and even the  $d$  and  $f$  block transition metals.

In addition, the energies of C atom under varying external charged environments are tested. Figure 2 shows that the triplet-singlet energy gaps by KS seriously deviate from the results of CCSDT, especially when the point charges are far away from the C atom. By comparison, HCKS significantly improves the performance of KS, in use of the same XC functionals. The occupations of the three  $p$  orbitals change gradually from [1,0,0] to [1/3, 1/3, 1/3] as the point charges move away from the C atom. Therefore, HCKS is able to capture the physical essence of strong correlation through dynamically varying occupations.

Besides the C atom, the triplet-singlet gaps of various atoms and diatoms from the TS12 benchmark set [71] are also calculated. For these systems, the ground states are triplets, while the lowest singlet states are of biradical character. More

TABLE I. Triplet-singlet gaps  $\Delta E_{T-S}$  ( $= E_S - E_T$ ) of various atoms and diatoms from the TS12 benchmark set [71]. Experimental data are used as reference. RKS, UKS, and HCKS with two XC functionals, BLYP and PBE, are tested. MSE and MAE stand for mean sign error and mean absolute error, respectively. Spin-unrestricted calculations are performed for triplet states, while spin-restricted calculations are performed for singlet states except UKS. All energies are in eV. The calculation results of RKS, UKS, and cRKS can be found in Ref. [24].

	Expt.	RKS		UKS		HCKS	
		BLYP	PBE	BLYP	PBE	BLYP	PBE
C	1.26	1.71	1.88	0.32	0.37	1.32	1.38
NF	1.49	1.85	1.97	0.44	0.47	1.44	1.48
NH	1.56	2.11	2.31	0.49	0.55	1.67	1.79
NO <sup>-</sup>	0.75	1.09	1.17	0.27	0.29	0.85	0.89
O <sub>2</sub>	0.98	1.57	1.63	0.37	0.38	1.14	1.15
O	1.97	2.69	2.89	0.65	0.70	1.83	1.90
PF	0.88	1.25	1.39	0.25	0.30	0.87	0.99
PH	0.95	1.32	1.50	0.26	0.34	0.92	1.09
S <sub>2</sub>	0.58	0.91	0.97	0.18	0.20	0.59	0.64
S	1.15	1.61	1.78	0.33	0.39	0.90	1.04
Si	0.78	1.07	1.25	0.18	0.26	0.69	0.86
SO	0.79	1.14	1.22	0.24	0.26	0.78	0.83
MSE		0.43	0.57	-0.76	-0.72	-0.01	0.07
MAE		0.43	0.57	0.76	0.72	0.08	0.10

tested details about TS12 can be found in Refs. [24,71]. Table I shows the test results of RKS, spin-unrestricted KS (UKS), and HCKS, in use of BLYP and PBE XC functionals. As above, RKS cannot capture the multireference nature of the singlet biradicals, because it provides a closed-shell solution for any singlet state. Therefore, the energies of the singlet states as well as the triplet-singlet gaps are systematically overestimated due to the lack of strong correlation. Unlike RKS, the destruction of spin symmetry in UKS leads to the over-relaxation of the orbitals occupied by the unpaired opposite-spin electrons, and thus the energies of the singlet states as well as the triplet-singlet gaps are underestimated. HCKS can correctly describe the strong correlation in singlet biradicals, and thus it predicts accurate energies of the singlet states and the MAEs of the triplet-singlet gaps by both BLYP and PBE are only 0.08 and 0.10 eV, respectively. Note that cRKS also has good performance for TS12 [24]; it embodies the singlet biradical character by two partially filled spin-restricted orbitals.

Here test also some atoms of 3d transition metals, which are generally considered to be a big challenge to KS. Due to the partially filled 3d subshell and the near degeneracy of 4s and 3d subshells, transition metals and systems containing them often have a plethora of low-lying degenerate and near-degenerate states, which make them much more difficult to correctly describe than main-group compounds. Figure 3 shows that KS with both PBE and BLYP XC functionals overestimates the energy gaps between high- and low-spin states of Cr, Fe, and Ni, due to the lack of strong correlation in the low-spin states. In contrast, HCKS improves the performance in use of the same XC functionals. The fractional

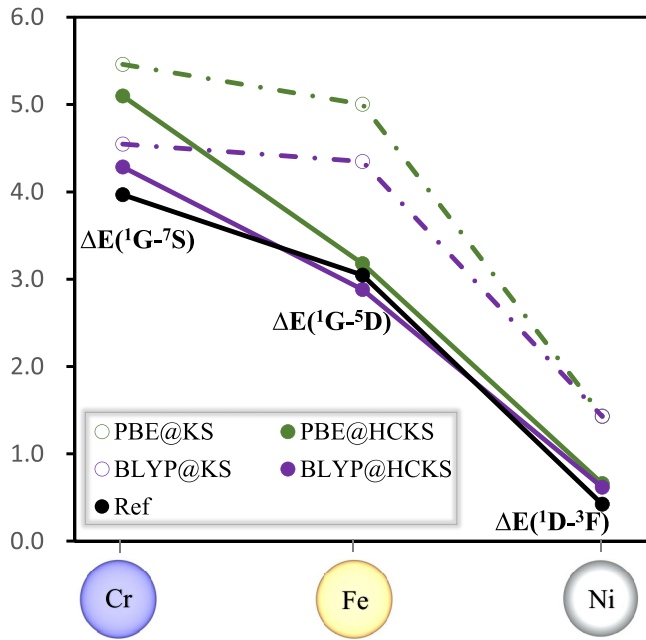


FIG. 3. Energy gaps between high- and low-spin states of transition metals. Septet-singlet, quintet-singlet, and triplet-singlet energy gaps for Cr, Fe, and Ni atoms, respectively, are calculated. KS and HCKS in use of the same XC functionals (PBE and BLYP) are examined, while the experimental data [80] are used as reference. For both KS and HCKS, spin-restricted and spin-unrestricted calculations are performed for low- and high-spin states, respectively. All energies are in eV.

occupations for (nearly) degenerate orbitals render the HCKS method the great potential to handle strong correlation. For example, PBE@HCKS converges to a set of spin-restricted orbitals for the singlet state of Ni, with occupations for both  $\alpha$  and  $\beta$  spins being 0.916 for each  $3d$  orbital and 0.420 for the  $4s$  orbital. This further proves that HCKS can improve the description of strong correlation while maintaining both spin and space symmetry.

Finally, a prototypical example of strongly correlated system, the stretched  $C_2$  molecule, is considered. Here the impact of different choices of XC functionals on the calculation of energies at bond dissociation limit is compared and evaluated to demonstrate the potential of HCKS in handling strong correlation. To this end, the PBE functional combined with different amounts of correction, i.e.,  $E_{XC}^{PBE} + c\Delta E_{XC}$ , is used, with  $c$  deciding the amount of correction in the XC functionals. The correction considered here takes the form of  $\Delta E_{XC} = E_X^{Dirac} - E_X^{TPSS}$ , with  $E_X^{Dirac}$  and  $E_X^{TPSS}$  being the Dirac [39] and TPSS [49] exchange functionals, respectively. It has been proved that  $E_X^{Dirac}$  includes not only the exchange energy but also some static correlation effect [48], while  $E_X^{TPSS}$  can better reproduce the exact exchange energy [81]. Thereby  $\Delta E_{XC}$  can be regarded as a correction of static correlation. By observing Fig. 4, it can be found that the overestimated energies at bond dissociation limit rarely change by KS with different amounts of correction, which emphasizes the difficulty of eliminating the systematical error of strong correlation within the framework of KS. In contrast, by adjusting  $c$  to include

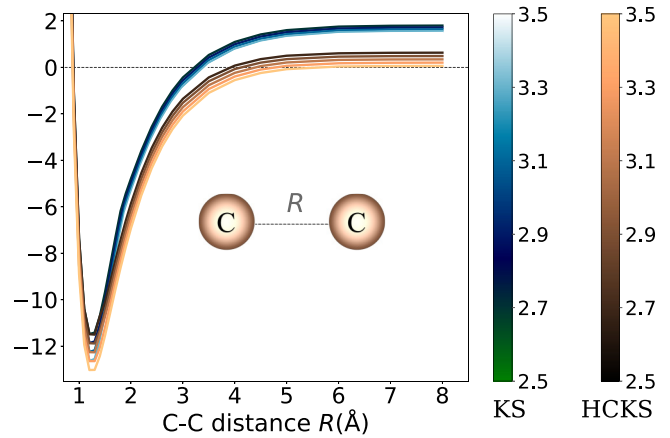


FIG. 4. Potential energy curves for C-C bond dissociation in  $C_2$ . The performances of KS and HCKS are evaluated in use of the PBE functional combined with different amounts of correction, that is,  $E_{XC}^{PBE} + c\Delta E_{XC}$ , with  $c$  deciding the amount of correction in the XC functionals. The correction takes the form of  $\Delta E_{XC} = E_X^{Dirac} - E_X^{TPSS}$ . Here the calculated energies with  $c$  ranging from 2.5 to 3.5 are plotted, and the total KS energies of two triplet C atoms are set to zero. All energies are in eV. By comparison, KS and HCKS predict the same energies at the equilibrium distance in use of the same functionals, while the overestimated energies rarely change in KS, which, however, can be effectively reduced by including appropriate amount of correction in HCKS. Note that the XC functionals used in this work are confined to semilocal functionals, similar results can be obtained if the nonlocal correction of  $\Delta E_{XC} = E_X^{Dirac} - E_X^{HF}$  is used instead.

appropriate amount of correction, the overestimated energies at bond dissociation limit can be effectively reduced. This thus indicates that HCKS creates new possibilities to address the issue of strong correlation in DFT. However, it should be noted that while the correction improves the energy of HCKS at the dissociation limit, it leads to the underestimation of the energy at the equilibrium distance by HCKS as well as KS. Moreover, HCKS cannot improve the calculation of KS-DFT for the simple stretched  $H_2$ , in use of functionals that explicitly depend only on the density. Therefore, further development of functionals that depend on  $\{\chi_p^\sigma\}$  and  $\{\lambda_p^\sigma\}$  is essential for the application of HCKS in strongly correlated systems.

## VI. CONCLUSIONS

This work presented theory to generalize KS-DFT to hypercomplex number systems. The resulting HCKS theory provides a general framework, and different dimensions of the HCKS orbitals lead to different HCKS methods, with KS-DFT and RDMFT being two cases corresponding to the smallest and largest dimensions. The test on the singlet biradical C atom shows that HCKS can maintain both spin and space symmetry for the density with equally occupied  $p$  orbitals, which cannot be achieved by KS. Besides, the predictions of the triplet-singlet gaps on the TS12 benchmark set, the energy gaps between high- and low-spin states for both transition metals and C atom under varying external charged environments, and the potential energy curve for  $C_2$  bond dissociation

demonstrate that HCKS is able to capture the multireference nature of strong correlation by dynamically varying fractional occupations, while KS in use of the same XC functionals cannot. Therefore, HCKS shows great potential to overcome the fundamental limitations of KS, which thus provides an alternative to the realization of DFT, and creates new channels for the development and evaluation of approximate functionals.

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