Theory and Functions in the Hypercomplex Kohn-Sham DFT Method

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The static/strong correlation error inherent in existing functionals has severely limited the further application of Kohn-Sham (KS) density functional theory (DFT). The recently developed hyper-complex KS (HCKS) theory shows great potential to overcome the fundamental limitations of the conventional KS-DFT, hence further development and application of HCKS will effectively guide the construction of new functionals toward better description of strong correlation. To this end, this work derives the working equations for the HCKS calculation and proves that HCKS using common functionals has much lower computational complexity than reduced density matrix functional theory (RDMFT), while maintaining the same density search space as RDMFT. Moreover, this work combines HCKS with hybrid functionals that are based on orbitals and their occupations. The test on triplet-singlet gaps shows that the systematic error of HCKS due to the lack of static correlation correction, while the large systematic errors of RKS and UKS rarely change with the correction. Therefore, HCKS creates new channels for the development and evaluation of approximate functionals, and the insights and advances gained in this work will be helpful to reduce the static correlation error in approximate functionals.

Kohn-Sham (KS) density functional theory (DFT) [1-5] is now the leading electronic structure method for both molecular and extended systems. Exact in principle, KS-DFT has to rely on density functional approximations (DFAs) to the exchange-correlation (XC) energy in practice. While existing DFAs have made the great success of KS-DFT, they cause notorious failures in practical applications [6-11], which severely limits the broader applicability of DFT.

The static/strong correlation issue is one of the most important and long-standing topic in DFT [12-16]. It has been proved that KS-DFT with commonly used DFAs, including local density approximations (LDAs), generalized gradient approximations (GGAs), meta-GGAs, and hybrid functionals, shows serious static correlation error [6,10,11,17]. Especially for systems where strong correlation becomes dominant, i.e. strongly correlated systems such as molecules with stretched bonds and Mott insulators, KS-DFT with common DFAs utterly fails [10]. Many efforts have been devoted toward systematic removal of the static correlation error inherent in approximate functionals [17-33]. Work from Becke showed some promise of describing strong correlation with XC hole modeling [30,31,35], based on which Johnson and Contreras-García constructed strong-correlation models for better description of atoms with fractional charges and spins [28,29]. It is worth mentioning that an effective fractional-spin correction was developed recently [17], which can restore the flat-plane behavior of electronic energy and properly describe the chemical bond dissociation without breaking spin symmetry. Nevertheless, the strong correlation problems that can be solved are very limited, and the progress to date is still far from being able to systematically eliminate the static correlation error in approximate functionals.

A recent effort proved that the generalizations of KS orbitals to hypercomplex number systems [36] can further extend the search space for the density in KS-DFT to a space that is equivalent to natural spin orbitals with fractional occupations in reduced density matrix functional theory (RDMFT [37,38]). The resulting Hypercomplex KS (HCKS) [36] is able to capture the multi-reference nature of strong correlation by optimized orbitals with dynamically varying fractional occupations. HCKS shows great potential to overcome the fundamental limitations of the conventional KS method, which thus creates new channels for the development and evaluation of approximation functionals.

The focus of this work is twofold. On the one hand, the theoretical framework of HCKS will be introduced in detail and extended to general functionals that depend on orbitals and their occupation numbers. On the other hand, this work seeks to gain in-depth insights into the development of approximate functionals through the comparison between KS and HCKS, in use of the same functionals that combine semi-local functionals with occupation-dependent Hartree-Fock (HF) like exchange. The advances in this work should be helpful for both the development and applications of DFT.

The total electronic energy in DFT is uniquely determined by the electronic density $E_{\text{tot}}[\rho_\sigma]$, which is further divided into the following four terms in the KS theory [2,3]

$$
E_{\text{tot}}[\rho_\sigma] = T_\sigma[\rho_\sigma] + E_{\text{ext}}[\rho_\sigma] + E_H[\rho_\sigma] + E_{\text{XC}}[\rho_\sigma],
$$

where $E_{\text{ext}}[\rho_\sigma]$ is the external energy

$$
E_{\text{ext}}[\rho_\sigma] = \sum_\sigma \int v_{\text{ext}}(\mathbf{r}) \rho_\sigma(\mathbf{r}) d\mathbf{r},
$$
The ground-state energy in KS can be obtained by the minimization of 
\[ E_{KH}[\rho_{\sigma}] = \frac{1}{2} \sum_{\alpha,\beta} \int \frac{\rho_{\sigma}(r_1)\rho_{\sigma}(r_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2, \]
and \( E_{XC}[\rho_{\sigma}] \) is the exchange-correlation (XC) energy, which is obtained by approximation in practice. \( T_s[\rho_{\sigma}] \) is the kinetic energy of the noninteracting reference system. Because the ground-state wave function of the noninteracting reference system is just a determinant, i.e., the KS determinant, \( T_s[\rho_{\sigma}] \) can be explicitly expressed in terms of the occupied KS orbitals \( \sigma \) [2][3],

\[ T_s[\rho_{\sigma}] = -\frac{1}{2} \sum_{\sigma} \sum_{k=1}^{N_{\sigma}} \bra{\varphi_k^\sigma} \nabla^2 \ket{\varphi_k^\sigma}, \]

while the Kohn-Sham ansatz guarantees that the exact ground state density can be written as the ground state density of the noninteracting reference,

\[ \rho_{\sigma}(\mathbf{r}) = \sum_{k=1}^{N_{\sigma}} |\varphi_k^\sigma(\mathbf{r})|^2. \]

The ground-state energy in KS can be obtained by the minimization of \( E_{tot}[\rho_{\sigma}] \) with respect to \{\( \varphi_k^\sigma \)\}, or equivalently, by solving the following KS equations

\[ \hat{h}^\sigma \varphi_k^\sigma(\mathbf{r}) = \varepsilon_k^\sigma \varphi_k^\sigma(\mathbf{r}), \]

where the KS operator is defined by

\[ \hat{h}^\sigma = -\frac{1}{2} \nabla^2 + v_\text{H}(\mathbf{r}) + v_\text{XC}(\mathbf{r}) + v_\text{ext}(\mathbf{r}), \]

and \( v_\text{H}(\mathbf{r}) \) and \( v_\text{XC}(\mathbf{r}) \) are the Coulomb and XC potentials, which are obtained via the functional derivatives \( \frac{\delta E_{\text{KH}}[\rho_{\sigma}]}{\delta \rho_{\sigma}(\mathbf{r})} \) and \( \frac{\delta E_{\text{XC}}[\rho_{\sigma}]}{\delta \rho_{\sigma}(\mathbf{r})} \) respectively.

In HCKS theory, the orbitals are formulated in hypercomplex number systems [30][31], which take the following form

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

where \( \{e_1, e_2, \ldots, e_n\} \) is a basis of dimension \( n \) in a Clifford algebra, such that \[ e_\mu^2 = -1; e_\mu e_\nu = -e_\nu e_\mu, \]

and \{\( \phi_p^{\sigma,\mu} \)\} is a set of real functions. The conjugate hypercomplex of Eq[8] takes the form of

\[ \varphi_p^\sigma(\mathbf{r}) = \phi_p^{\sigma,0}(\mathbf{r}) - \sum_{\mu=1}^{n} \phi_p^{\sigma,\mu}(\mathbf{r}) e_\mu. \]

The HCKS orbitals are a set of general KS orbitals of high dimension, and the determinant constructed by occupied HCKS orbitals is called the HCKS determinant.

Although the HCKS orbitals and HCKS determinant are hypercomplex, the resulting density and kinetic energy are real, which can be obtained by inserting Eq[8] into Eqs[5] and[4] respectively. They are

\[ \rho_{\sigma}(\mathbf{r}) = \sum_{k=1}^{N_{\sigma}} |\phi_k^{\sigma,0}(\mathbf{r})|^2, \]

and

\[ T_s[\rho_{\sigma}] = -\frac{1}{2} \sum_{\sigma} \sum_{k=1}^{N_{\sigma}} \sum_{\mu=1}^{n} \langle \phi_k^{\sigma,\mu} | \nabla^2 | \phi_k^{\sigma,\mu} \rangle. \]

Thereby, based on the HCKS orbitals defined by Eq[8] the energy of Eq[1] remains real. The minimization of \( E_{tot}[\rho_{\sigma}] \) with respect to the HCKS orbitals leads to a set of high-dimension KS equations, named the HCKS equations,

\[ \begin{cases} \hat{h}^\sigma \phi_p^{\sigma,0}(\mathbf{r}) = \varepsilon_p^\sigma \phi_p^{\sigma,0}(\mathbf{r}) \\ \hat{h}^\sigma \phi_p^{\sigma,1}(\mathbf{r}) = \varepsilon_p^\sigma \phi_p^{\sigma,1}(\mathbf{r}) \\ \vdots \\ \hat{h}^\sigma \phi_p^{\sigma,n}(\mathbf{r}) = \varepsilon_p^\sigma \phi_p^{\sigma,n}(\mathbf{r}). \end{cases} \]

It can be deduced from Eq[13] that all nonzero \( \phi_p^{\sigma,\mu} \) for \( \mu = 0 - n \) are the eigenvectors of \( \hat{h}^\sigma \) with the same eigenvalue \( \varepsilon_p^\sigma \). When the eigenvector associated with \( \varepsilon_p^\sigma \) is not degenerate, the components \( \phi_p^{\sigma,\mu} \) in the \( \mu \)-th HCKS orbital are either 0 or different only by a constant factor; while for the degenerate case, degenerate eigenvectors and their mix can appear in different components of the \( \mu \)-th HCKS orbital, which can lead to fractional occupations for each degenerate eigenvector.

Instead of solving Eq[13] \( \{\phi_p^{\sigma,\mu}\} \) can be further expanded on a set of orthonormal functions \( \{\chi_p^\sigma\} \)

\[ \phi_p^{\sigma,\mu}(\mathbf{r}) = \sum_{q=1}^{K} \chi_q^\sigma(\mathbf{r}) V^{\sigma,\mu}_{pq}, \]

where \( V^{\sigma,\mu} \) is a \( K \times K \) matrix associated with the \( \mu \)-th component of the HCKS orbitals. With this, the density of Eq[14] becomes,

\[ \rho_{\sigma}(\mathbf{r}) = \sum_{p,q=1}^{K} \chi_p^\sigma(\mathbf{r}) D^{\sigma}_{pq} \chi_q^\sigma(\mathbf{r}), \]

and \( D^{\sigma} \) is the density matrix on \( \{\chi_p^\sigma\} \)

\[ D^{\sigma} = \sum_{\mu=0}^{n} V^{\sigma,\mu T} \Gamma_N^{\sigma} V^{\sigma,\mu}, \]

where \( \Gamma_N^{\sigma} \) is a \( K \times K \) diagonal matrix, with the first \( N_{\sigma} \) diagonal elements being 1 and the rest being 0. Because \( D^{\sigma} \) is symmetric, it can be diagonalized by an orthogonal matrix \( U^{\sigma} \),

\[ D^{\sigma} = U^{\sigma} \Lambda^{\sigma} U^{\sigma T}, \]
where $\Lambda^\sigma$ is a diagonal matrix, $\text{diag}(\lambda_1^\sigma, \lambda_2^\sigma, \ldots, \lambda_K^\sigma)$, and $\{\chi_k^\sigma\}$ are the eigenvalues of $D^\sigma$. By inserting Eq [17] the density of Eq [18] can be further formulated as

$$\rho_{\sigma}(r) = \sum_{p=1}^{K} \lambda_p^\sigma |\chi_p^\sigma(r)|^2. \quad (18)$$

Here $\{\chi_k^\sigma\}$ are obtained via the unitary transformation on $\{\chi_k\}$: $\chi_p^\sigma(r) = \sum_{q=1}^{K} \chi_q(r) U_{qp}^\sigma$, which guarantees that $\{\chi_k^\sigma\}$ are orthonormal. The kinetic energy in HCKS is obtained by inserting Eqs [14], [16] and [17] into Eq [12] which takes the form

$$T_h[\rho_\sigma] = -\frac{1}{2} \sum_{\sigma} \sum_{p=1}^{K} \lambda_p^\sigma |\nabla |\chi_p^\sigma|_p^2. \quad (19)$$

The ground-state energy can be obtained by the minimization of $E_{\text{tot}}[\rho_\sigma]$ with respect to both $\{\chi_p^\sigma\}$ and $\{\lambda_p^\sigma\}$, subject to

$$\langle \psi_p^\sigma | \psi_q^\sigma \rangle = \delta_{pq}; 0 \leq n_p^\sigma \leq 1, \sum_{p=1}^{K} n_p^\sigma = N_\sigma. \quad (20)$$

In practice, the minimization is performed repeatedly on $\{\chi_p^\sigma\}$ and $\{\lambda_p^\sigma\}$ respectively, until the changes for both $\{\chi_p^\sigma\}$ and $\{\lambda_p^\sigma\}$ are small between two iterations. Of both minimization procedures, the minimization process for $\{\chi_p^\sigma\}$ is more computational complexity. Different from RDMFT using costly gradient algorithms, the minimization with respect to $\{\chi_p^\sigma\}$ in HCKS can be achieved via the following eigenvalue equations

$$\hat{h}^\sigma \chi_p^\sigma(r) = \varepsilon_p^\sigma \chi_p^\sigma(r), \quad (21)$$

which greatly reduces the computational cost of HCKS as compared to RDMFT. Note that although Eq [21] has the same form as Eq [6] in use of the same XC functional, HCKS allows dynamically varying fractional occupations which can result in a different density from KS, leading to different $\hat{h}^\sigma$ and eigenvectors.

The XC functionals in HCKS can be semi-local pure density functionals, or functionals that implicitly depend on the density through $\{\chi_p^\sigma\}$ and $\{\lambda_p^\sigma\}$. Based on $\{\chi_p^\sigma\}$ and $\{\lambda_p^\sigma\}$, the Hartree-Fock like (HF-like) exchange becomes

$$E_{\text{HF}} = -\frac{1}{2} \sum_{\sigma} \sum_{k,l} N_\sigma \int \chi_k^\sigma(r_1) \chi_l^\sigma(r_2) \chi_l^\sigma(r_2) \chi_k^\sigma(r_1) \frac{1}{r_{12}^2} dr_1 dr_2. \quad (22)$$

Similarly, the long-range and short-range HF-like exchange functionals can be defined by including the error function erf($\omega_{r_{12}}$) and the complementary error function erf($\omega_{r_{12}}$) in Eq [22]. With these, the global hybrid functionals $[11, 49]$ and all kinds of long-range corrected hybrid functionals $[47, 60]$ in KS can be applied in HCKS as well. The ground-state energy of HCKS with hybrid functionals can be obtained via the similar procedure described above, except that the XC potential in $\hat{h}^\sigma$ of Eq [21] becomes delocalized, which includes the HF-like exchange potential

$$v_{\text{HF}}(r_1, r_2) = -\sum_{k} n_k^\sigma \chi_k^\sigma(r_1) \chi_k^\sigma(r_2) \frac{1}{r_{12}}. \quad (23)$$

Similarly, the long-range and short-range parts of the HF-like exchange potential can be defined correspondingly.

Here the spin-restricted KS (RKS), spin-unrestricted (UKS), and HCKS in use of the same semi-local and hybrid functionals will be evaluated on the recent developed TS12 benchmark set $[61]$. This dataset includes 12 data points for triplet-singlet gaps of several atoms and diatomic molecules. The ground states of these systems are triplets, while the lowest singlet states are of biradical character. More test details about TS12 can be found in refs $[61, 62]$. The XC functionals applied here are the nonempirical meta-GGA TPSS $[63]$ and the hybrid functionals based on TPSS. All calculations were performed using a local modified version of the NWChem package $[64]$.

The test results of the semi-local functional TPSS can be found in Tab 1. As can be seen that TPSS@RKS systematically overestimates the triplet-singlet gaps of the 12 systems in TS12. Due to the limitation of RKS, TPSS@RKS can only provide a closed-shell solution for any singlet state, with all orbitals either doubly occupied or empty. Thereby, it cannot capture the multi-reference nature of the singlet biradicals, resulting in overestimation of the energies of the lowest singlet states. Note that even though RKS can correctly predict the zero spin-densities ($\rho_{\alpha} - \rho_{\beta}$) for these singlets, it breaks the space symmetry of the total densities $[61, 62]$. Unlike TPSS@RKS, TPSS@UKS can predict the biradical character by breaking the spin symmetry, with two unpaired electrons of opposite spins confined in different physical region. However, the destruction of spin symmetry leads to the over-relaxation of the orbitals occupied by the unpaired opposite electrons, thus the energies of the singlet states as well as the triplet-singlet gaps are systematically underestimated. Similar results and discussions about RKS and UKS can be found in ref $[62]$. In contrast, HCKS allows dynamically varying fractional occupations to capture the multi-reference nature of strong correlation. Hence, TPSS@HCKS significantly improves the predicted triplet-singlet gaps, with the error of TPSS@RKS reduced by half. Even so, the triplet-singlet gaps are still systematically overestimated due to the lack of static correlation in TPSS, both MSE and MAE are 7.27 kcal/mol. Actually, this error can be reduced to 2.41 kcal/mol when the PBE XC functional $[65]$ is used. Therefore, approximate functionals to the XC energy has a large influence on the calculation of
HCKS, which will be further explored below.

In order to effectively guide the development of functionals toward better description of strong correlation, it is essential to further compare and evaluate the impact of different choices of XC functional on RKS, UKS, and HCKS when calculating systems of multi-reference nature. To this end, the triplet-singlet gaps of TS12 are calculated by RKS, UKS, and HCKS when calculating systems of multi-reference interaction ∆ \( E_{X} \), where ∆ \( E_{X} \) has little impact on both RKS and UKS. The systematic errors of hTPSS@RKS and hTPSS@UKS rarely change for different \( c_{HF}^{X} \). In fact, similar results can be obtained by other hybrid functionals based on LDAs, GGAs, and meta-GGAs. This thus indicates that the description of strong correlation poses a great challenge to DFT within the frameworks of RKS and UKS, and explains the slow progress in systematically eliminating the strong correlation error inherent in commonly used DFAs.

In summary, this work presented the main equations for the calculation of the HCKS theory. The derivation shows that the computational complexity of HCKS can be greatly reduced by solving a set of eigenvalue equations instead of applying the gradient algorithms that are used in RDMFT, for minimizing the energy with respect to orbitals. Therefore, in used of common functionals, HCKS can have the same search space for the density matrix as KS, while maintaining the same computational scaling as KS. In addition, this work further combined HCKS with hybrid functionals that are based on orbitals and their occupations. The test on the triplet-singlet gaps of the TS12 benchmark set shows that although HCKS allows dynamically varying fractional occupations to capture the multi-reference nature of strong correlation, its test results largely depend on the choice of approximate functionals. In particular, the systematic error of HCKS due to the lack of static correlation in approximate functionals can be effectively reduced by including appropriate amount of the static correlation correction

| RKS | UKS | HCKS |
|-----|-----|------|
| Expt. | TPSS hTPSS | TPSS hTPSS | TPSS hTPSS |
| C    | 29.14 | 42.28 | 41.80 | 5.22 | 4.88 | 40.59 | 31.34 |
| NF   | 34.32 | 46.09 | 45.25 | 9.52 | 9.16 | 40.61 | 32.13 |
| NH   | 35.93 | 56.03 | 55.71 | 14.11 | 13.97 | 50.22 | 42.01 |
| NO   | 17.30 | 27.79 | 26.90 | 6.12 | 5.80 | 24.50 | 17.78 |
| O    | 22.64 | 37.51 | 36.80 | 7.38 | 6.96 | 31.03 | 22.38 |
| O    | 45.37 | 68.80 | 68.41 | 17.28 | 17.11 | 55.63 | 42.34 |
| PF   | 20.27 | 32.67 | 32.21 | 5.98 | 5.88 | 26.11 | 20.70 |
| PH   | 21.90 | 35.65 | 35.37 | 7.57 | 7.50 | 28.95 | 23.67 |
| S    | 13.44 | 23.08 | 22.65 | 4.16 | 4.00 | 17.21 | 12.13 |
| S    | 26.41 | 42.06 | 41.72 | 8.85 | 8.79 | 29.29 | 20.85 |
| Si   | 18.01 | 28.64 | 28.40 | 7.59 | 7.50 | 28.95 | 23.67 |
| SO   | 18.16 | 28.52 | 27.96 | 5.16 | 4.91 | 22.24 | 16.04 |
| MSE  | 13.85 | 13.36 | 17.26 | 17.47 | 7.27 | -0.30 |
| MAE  | 13.85 | 13.36 | 17.26 | 17.47 | 7.27 | 2.13 |
(i.e. $E_{\text{DFA}} - E_{\text{HF}}$). Unlike HCKS, RKS and UKS show even large systematic errors on the triplet-singlet gaps, worse still, the errors rarely change with the correction of static correction. Therefore, HCKS provides a feasible approach toward the strong correlation problem, the insights and advances gained in this work will be helpful in the development and evaluation of approximation functionals.

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