Supplementary Information for

Describing Strong Correlation with Fractional-Spin Correction in Density Functional Theory

Neil Qiang Su, Chen Li and Weitao Yang

Weitao Yang.
E-mail: weitao.yang@duke.edu

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Supporting Information Text

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1. Energy corrections for systems with fractional charges and fractional spins

The DFT total electronic energy (1, 2) is

$$E_{\text{Tot}} = T_{\text{S}} + E_{\text{ext}} + J + E_{\text{XC}}, \tag{S1}$$

where the four terms on the right side are the kinetic energy, the external potential energy, the electron-electron Coulomb repulsion energy, and the exchange-correlation (XC) energy, respectively.

For a system with N^α (equal to $N_0^\alpha + \Delta N^\alpha$) alpha and N^β (equal to $N_0^\beta + \Delta N^\beta$) beta electrons, where ΔN^α and ΔN^β are the fractional parts of the electron numbers, the total electronic energy should obey the flat-plane condition (3), i.e., the energy, as a function of ΔN^α and ΔN^β, is two flat planes intersecting in the seam of $\Delta N^\alpha + \Delta N^\beta = 1$, which is

$$\begin{aligned}\tilde{E}_{\text{Tot}}(N^\alpha, N^\beta) =& (1 - \Delta N^\alpha - \Delta N^\beta) E_{\text{Tot}}(N_0^\alpha, N_0^\beta) + \Delta N^\alpha E_{\text{Tot}}(N_0^\alpha + 1, N_0^\beta) \\ &+ \Delta N^\beta E_{\text{Tot}}(N_0^\alpha, N_0^\beta + 1)\end{aligned} \tag{S2}$$

for $0 \le \Delta N^\alpha + \Delta N^\beta \le 1$;

$$\begin{aligned}\tilde{E}_{\text{Tot}}(N^\alpha, N^\beta) =& (\Delta N^\alpha + \Delta N^\beta - 1) E_{\text{Tot}}(N_0^\alpha + 1, N_0^\beta + 1) + (1 - \Delta N^\beta) E_{\text{Tot}}(N_0^\alpha + 1, N_0^\beta) \\ &+ (1 - \Delta N^\alpha) E_{\text{Tot}}(N_0^\alpha, N_0^\beta + 1)\end{aligned} \tag{S3}$$

for $1 < \Delta N^\alpha + \Delta N^\beta \le 2$.

Similar to the corrections for systems with fractional charges derived by imposing the linearity condition (4) on each component of Kohn-Sham (KS) DFT energy (5), the corrections for systems with both fractional charges and fractional spins can be obtained by imposing the flat-plane condition on each component. With the integer points kept intact, the flat-plane counterpart for each component, $\tilde{E}_{\text{comp}}$, is constructed in a form similar to that of total energy (Eqs. S2 and S3). The deviation from the flat-plane counterpart for each component of the total energy can be obtained by

$$\Delta E_{\text{comp}}(N^\alpha, N^\beta) = \tilde{E}_{\text{comp}}(N^\alpha, N^\beta) - E_{\text{comp}}(N^\alpha, N^\beta). \tag{S4}$$

By adding all the deviations from each component together, we obtain

$$\begin{aligned}&\Delta T_{\text{S}}(N^\alpha, N^\beta) + \Delta E_{\text{ext}}(N^\alpha, N^\beta) + \Delta J(N^\alpha, N^\beta) + \Delta E_{\text{XC}}(N^\alpha, N^\beta) \\ &= \tilde{T}_{\text{S}}(N^\alpha, N^\beta) - T_{\text{S}}(N^\alpha, N^\beta) + \tilde{E}_{\text{ext}}(N^\alpha, N^\beta) - E_{\text{ext}}(N^\alpha, N^\beta) \\ &+ \tilde{J}(N^\alpha, N^\beta) - J(N^\alpha, N^\beta) + \tilde{E}_{\text{XC}}(N^\alpha, N^\beta) - E_{\text{XC}}(N^\alpha, N^\beta) \\ &= \tilde{T}_{\text{S}}(N^\alpha, N^\beta) + \tilde{E}_{\text{ext}}(N^\alpha, N^\beta) + \tilde{J}(N^\alpha, N^\beta) + \tilde{E}_{\text{XC}}(N^\alpha, N^\beta) \\ &- T_{\text{S}}(N^\alpha, N^\beta) - E_{\text{ext}}(N^\alpha, N^\beta) - J(N^\alpha, N^\beta) - E_{\text{XC}}(N^\alpha, N^\beta) \\ &= \tilde{E}_{\text{Tot}}(N^\alpha, N^\beta) - E_{\text{Tot}}(N^\alpha, N^\beta) \\ &= \Delta E_{\text{Tot}}(N^\alpha, N^\beta).\end{aligned} \tag{S5}$$

Here, we have made use of the relation that the flat-plane counterparts for the four components add up to the two flat planes of the total energy, i.e. $\tilde{E}_{\text{Tot}}(N^\alpha, N^\beta) = \tilde{T}_{\text{S}}(N^\alpha, N^\beta) + \tilde{E}_{\text{ext}}(N^\alpha, N^\beta) + \tilde{J}(N^\alpha, N^\beta) + \tilde{E}_{\text{XC}}(N^\alpha, N^\beta)$, which is correct because the flat-plane counterparts, for the four components and the total energy, are uniquely determined once the integer points are fixed, and they are constructed with the integer points kept intact. Eq. S5 shows that the correction for the total energy can be obtained by adding up the deviations of each component from the flat-plane counterpart, which means that sufficient conditions for the flat-plane condition are imposed as was first demonstrated for the fractional charge correction (5).

With frozen-orbital assumption, both the kinetic energy and the external potential energy are linear functions of ΔN^α and ΔN^β, thus no correction is needed for these two components. Only those corrections from nonlinear functions, i.e., the electron-electron Coulomb repulsion energy $J[\rho]$, the Hartree-Fock (HF) exchange energy $E_{\text{X}}^{\text{HF}}[\rho_s]$, and XC density functionals $E_{\text{XC}}^{\text{DFA}}[\rho]$, are needed, which will be derived in the rest of this section. In this section, we assume that all canonical orbitals (COs) are occupied by integer (0 or 1) alpha and beta electrons, except that the f-th orbital is fractionally occupied, whose occupations are n_f^α and n_f^β. Spin-restricted self-consistent field (SCF) (2, 6, 7) is used throughout the derivations and calculations in this paper, therefore the spacial functions of both alpha and beta COs are the same, they are indicated as $\{\varphi_p\}$ in the following derivations.

It should be noted that different realizations of (generalized) KS methods are available (8, 9), such as spin-restricted and spin-unrestricted methods. In spin-unrestricted method, the resulting Slater determinant is not necessarily a pure eigenfunction of the square of total spin, $\hat{S}^2$, which may be "contaminated" by other spin states. In contrast, spin-restricted method restricts the reference Slater determinant to be an eigenfunction of $\hat{S}^2$, which allows the wavefunction to possess the physically correct spin symmetry. Thus, spin-restricted method is frequently used when the exact symmetry properties are crucial for understanding the chemical and physical behavior of the system under study. However, for spin-restricted method, the spin density is determined only by the singly occupied orbitals and thus has the same sign at every point in space, which can be incorrect for some open-shell systems whose spin densities are of different signs in different regions (9–12). In comparison, spin-unrestricted method in principle allows a broken-symmetry solution to better describe the spin density for open-shell systems or systems in an external magnetic field; in addition, it should be able to give the spin-restricted solution when the energy is lower. Therefore, both spin-restricted and spin-unrestricted methods are important in practical applications of DFT.

A. The correction to the Coulomb repulsion energy. The Coulomb repulsion energy with fractional occupations is

$$\begin{aligned}
J\left[\rho^\alpha_{N_0^\alpha+n_f^\alpha},\rho^\beta_{N_0^\beta+n_f^\beta}\right] &= \frac{1}{2}\iint \frac{\left[\rho^\alpha_{N_0^\alpha+n_f^\alpha}(\mathbf{r})+\rho^\beta_{N_0^\beta+n_f^\beta}(\mathbf{r})\right]\left[\rho^\alpha_{N_0^\alpha+n_f^\alpha}(\mathbf{r}')+\rho^\beta_{N_0^\beta+n_f^\beta}(\mathbf{r}')\right]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \\
&= \frac{1}{2}\iint \frac{\left[\rho^\alpha_{N_0^\alpha}(\mathbf{r})+n_f^\alpha\rho_f(\mathbf{r})+\rho^\beta_{N_0^\beta}(\mathbf{r})+n_f^\beta\rho_f(\mathbf{r})\right]\left[\rho^\alpha_{N_0^\alpha}(\mathbf{r}')+n_f^\alpha\rho_f(\mathbf{r}')+\rho^\beta_{N_0^\beta}(\mathbf{r}')+n_f^\beta\rho_f(\mathbf{r}')\right]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \\
&= J\left[\rho^\alpha_{N_0^\alpha},\rho^\beta_{N_0^\beta}\right]+(n_f^\alpha+n_f^\beta)\iint \frac{\rho_f(\mathbf{r})\left[\rho^\alpha_{N_0^\alpha}(\mathbf{r}')+\rho^\beta_{N_0^\beta}(\mathbf{r}')\right]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+\frac{1}{2}(n_f^\alpha+n_f^\beta)^2\iint\frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'.
\end{aligned} \tag{S6}$$

Here $\rho^\sigma_{N^\sigma}(\mathbf{r})$ is the density of σ spin and $\rho_f(\mathbf{r})$ is the density of Orbital f, $|\varphi_f(\mathbf{r})|^2$. As Eq. S6 is a quadratic function of n_f^α and n_f^β, the correction can be exactly derived. The flat-plane counterpart is

$$\begin{aligned}
\tilde{J}\left[\rho^\alpha_{N_0^\alpha+n_f^\alpha},\rho^\beta_{N_0^\beta+n_f^\beta}\right] &= (1-n_f^\alpha-n_f^\beta)J\left[\rho^\alpha_{N_0^\alpha},\rho^\beta_{N_0^\beta}\right]+n_f^\alpha J\left[\rho^\alpha_{N_0^\alpha+1},\rho^\beta_{N_0^\beta}\right]+n_f^\beta J\left[\rho^\alpha_{N_0^\alpha},\rho^\beta_{N_0^\beta+1}\right] \\
&= (1-n_f^\alpha-n_f^\beta)J\left[\rho^\alpha_{N_0^\alpha},\rho^\beta_{N_0^\beta}\right] \\
&\quad + n_f^\alpha\left\{J\left[\rho^\alpha_{N_0^\alpha},\rho^\beta_{N_0^\beta}\right]+\iint\frac{\rho_f(\mathbf{r})\left[\rho^\alpha_{N_0^\alpha}(\mathbf{r}')+\rho^\beta_{N_0^\beta}(\mathbf{r}')\right]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+\frac{1}{2}\iint\frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\right\} \\
&\quad + n_f^\beta\left\{J\left[\rho^\alpha_{N_0^\alpha},\rho^\beta_{N_0^\beta}\right]+\iint\frac{\rho_f(\mathbf{r})\left[\rho^\alpha_{N_0^\alpha}(\mathbf{r}')+\rho^\beta_{N_0^\beta}(\mathbf{r}')\right]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+\frac{1}{2}\iint\frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\right\} \\
&= J\left[\rho^\alpha_{N_0^\alpha},\rho^\beta_{N_0^\beta}\right]+(n_f^\alpha+n_f^\beta)\iint\frac{\rho_f(\mathbf{r})\left[\rho^\alpha_{N_0^\alpha}(\mathbf{r}')+\rho^\beta_{N_0^\beta}(\mathbf{r}')\right]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+\frac{1}{2}(n_f^\alpha+n_f^\beta)\iint\frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'
\end{aligned} \tag{S7}$$

for $0\le n_f^\alpha+n_f^\beta\le 1$;

$$\begin{aligned}
\tilde{J}\left[\rho^\alpha_{N_0^\alpha+n_f^\alpha},\rho^\beta_{N_0^\beta+n_f^\beta}\right] &= (n_f^\alpha+n_f^\beta-1)J\left[\rho^\alpha_{N_0^\alpha+1},\rho^\beta_{N_0^\beta+1}\right]+(1-n_f^\beta)J\left[\rho^\alpha_{N_0^\alpha+1},\rho^\beta_{N_0^\beta}\right]+(1-n_f^\alpha)J\left[\rho^\alpha_{N_0^\alpha},\rho^\beta_{N_0^\beta+1}\right] \\
&= (n_f^\alpha+n_f^\beta-1)\left\{J\left[\rho^\alpha_{N_0^\alpha},\rho^\beta_{N_0^\beta}\right]+2\iint\frac{\rho_f(\mathbf{r})\left[\rho^\alpha_{N_0^\alpha}(\mathbf{r}')+\rho^\beta_{N_0^\beta}(\mathbf{r}')\right]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+2\iint\frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\right\} \\
&\quad +(1-n_f^\beta)\left\{J\left[\rho^\alpha_{N_0^\alpha},\rho^\beta_{N_0^\beta}\right]+\iint\frac{\rho_f(\mathbf{r})\left[\rho^\alpha_{N_0^\alpha}(\mathbf{r}')+\rho^\beta_{N_0^\beta}(\mathbf{r}')\right]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+\frac{1}{2}\iint\frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\right\} \\
&\quad +(1-n_f^\alpha)\left\{J\left[\rho^\alpha_{N_0^\alpha},\rho^\beta_{N_0^\beta}\right]+\iint\frac{\rho_f(\mathbf{r})\left[\rho^\alpha_{N_0^\alpha}(\mathbf{r}')+\rho^\beta_{N_0^\beta}(\mathbf{r}')\right]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+\frac{1}{2}\iint\frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\right\} \\
&= J\left[\rho^\alpha_{N_0^\alpha},\rho^\beta_{N_0^\beta}\right]+(n_f^\alpha+n_f^\beta)\iint\frac{\rho_f(\mathbf{r})\left[\rho^\alpha_{N_0^\alpha}(\mathbf{r}')+\rho^\beta_{N_0^\beta}(\mathbf{r}')\right]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+\frac{1}{2}(3n_f^\alpha+3n_f^\beta-2)\iint\frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'
\end{aligned} \tag{S8}$$

for $1< n_f^\alpha+n_f^\beta\le 2$. The correction to the Coulomb energy is thus obtained from the difference, $\tilde{J}-J$, which is

$$\begin{aligned}
\Delta J\left[\rho^\alpha_{N_0^\alpha+n_f^\alpha},\rho^\beta_{N_0^\beta+n_f^\beta}\right] &= \frac{(n_f^\alpha+n_f^\beta)-(n_f^\alpha+n_f^\beta)^2}{2}\iint\frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \\
&= \left[\frac{(n_f^\alpha-n_f^{\alpha 2})+(n_f^\beta-n_f^{\beta 2})}{2}-n_f^\alpha n_f^\beta\right]\iint\frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'
\end{aligned} \tag{S9}$$

for $0\le n_f^\alpha+n_f^\beta\le 1$;

$$\begin{aligned}
\Delta J\left[\rho^\alpha_{N_0^\alpha+n_f^\alpha},\rho^\beta_{N_0^\beta+n_f^\beta}\right] &= \frac{(3n_f^\alpha+3n_f^\beta-2)-(n_f^\alpha+n_f^\beta)^2}{2}\iint\frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \\
&= \left[\frac{(n_f^\alpha-n_f^{\alpha 2})+(n_f^\beta-n_f^{\beta 2})}{2}-(1-n_f^\alpha)(1-n_f^\beta)\right]\iint\frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'
\end{aligned} \tag{S10}$$

for $1< n_f^\alpha+n_f^\beta\le 2$. Eqs. S9 and S10 can be merged into

$$\Delta J\left[\rho^\alpha_{N_0^\alpha+n_f^\alpha},\rho^\beta_{N_0^\beta+n_f^\beta}\right] = \frac{(n_f^\alpha-n_f^{\alpha 2})+(n_f^\beta-n_f^{\beta 2})}{2}\iint\frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'-\Lambda(n_f^\alpha,n_f^\beta)\iint\frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \tag{S11}$$

where

$$\Lambda(n_f^\alpha, n_f^\beta) = \begin{cases} n_f^\alpha n_f^\beta, & n_f^\alpha + n_f^\beta \le 1 \\ (1-n_f^\alpha)(1-n_f^\beta), & n_f^\alpha + n_f^\beta > 1. \end{cases} \quad \text{[S12]}$$

The two terms on the rhs of Eq. S11 correspond to same-spin and opposite-spin contributions respectively.

B. The correction to the Hartree-Fock exchange energy. The HF exchange energy with fractional occupations is

$$\begin{aligned} E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha+n_f^\alpha}^\alpha, \rho_{s,N_0^\beta+n_f^\beta}^\beta\right] &= -\frac{1}{2}\sum_\sigma \iint \frac{\rho_{s,N_0^\sigma+n_f^\sigma}^\sigma(\mathbf{r},\mathbf{r}')\rho_{s,N_0^\sigma+n_f^\sigma}^\sigma(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \\ &= -\frac{1}{2}\sum_\sigma \iint \frac{\left[\rho_{s,N_0^\sigma}^\sigma(\mathbf{r},\mathbf{r}') + n_f^\sigma \rho_{s,f}(\mathbf{r},\mathbf{r}')\right]\left[\rho_{s,N_0^\sigma}^\sigma(\mathbf{r}',\mathbf{r}) + n_f^\sigma \rho_{s,f}(\mathbf{r}',\mathbf{r})\right]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \\ &= E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha}^\alpha, \rho_{s,N_0^\beta}^\beta\right] - \sum_\sigma n_f^\sigma \iint \frac{\rho_{s,f}(\mathbf{r},\mathbf{r}')\rho_{s,N_0^\sigma}^\sigma(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' - \frac{1}{2}\sum_\sigma n_f^{\sigma 2} \iint \frac{\rho_{s,f}(\mathbf{r},\mathbf{r}')\rho_{s,f}(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \\ &= E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha}^\alpha, \rho_{s,N_0^\beta}^\beta\right] - \sum_\sigma n_f^\sigma \iint \frac{\rho_{s,f}(\mathbf{r},\mathbf{r}')\rho_{s,N_0^\sigma}^\sigma(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' - \frac{1}{2}\sum_\sigma n_f^{\sigma 2} \iint \frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \quad \text{[S13]} \end{aligned}$$

Here $\rho_{s,N^\sigma}^\sigma(\mathbf{r},\mathbf{r}')$ is the reduced single-electron density matrix of σ spin and $\rho_{s,f}(\mathbf{r},\mathbf{r}')$ is the density matrix of Orbital f, $\varphi_f(\mathbf{r})\varphi_f^*(\mathbf{r}')$. Similarly, the flat-plane counterpart of the HF exchange energy is

$$\begin{aligned} &\tilde{E}_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha+n_f^\alpha}^\alpha, \rho_{s,N_0^\beta+n_f^\beta}^\beta\right] \\ &= (1-n_f^\alpha-n_f^\beta)E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha}^\alpha, \rho_{s,N_0^\beta}^\beta\right] + n_f^\alpha E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha+1}^\alpha, \rho_{s,N_0^\beta}^\beta\right] + n_f^\beta E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha}^\alpha, \rho_{s,N_0^\beta+1}^\beta\right] \\ &= (1-n_f^\alpha-n_f^\beta)E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha}^\alpha, \rho_{s,N_0^\beta}^\beta\right] \\ &+ n_f^\alpha\left\{E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha}^\alpha, \rho_{s,N_0^\beta}^\beta\right] - \iint \frac{\rho_{s,f}(\mathbf{r},\mathbf{r}')\rho_{s,N_0^\alpha}^\alpha(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' - \frac{1}{2}\iint \frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\right\} \\ &+ n_f^\beta\left\{E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha}^\alpha, \rho_{s,N_0^\beta}^\beta\right] - \iint \frac{\rho_{s,f}(\mathbf{r},\mathbf{r}')\rho_{s,N_0^\beta}^\beta(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' - \frac{1}{2}\iint \frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\right\} \\ &= E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha}^\alpha, \rho_{s,N_0^\beta}^\beta\right] - \sum_\sigma n_f^\sigma \iint \frac{\rho_{s,f}(\mathbf{r},\mathbf{r}')\rho_{s,N_0^\sigma}^\sigma(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' - \frac{1}{2}\sum_\sigma n_f^\sigma \iint \frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \quad \text{[S14]} \end{aligned}$$

for $0 \le n_f^\alpha + n_f^\beta \le 1$;

$$\begin{aligned} &\tilde{E}_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha+n_f^\alpha}^\alpha, \rho_{s,N_0^\beta+n_f^\beta}^\beta\right] \\ &= (n_f^\alpha+n_f^\beta-1)E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha+1}^\alpha, \rho_{s,N_0^\beta+1}^\beta\right] + (1-n_f^\beta)E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha+1}^\alpha, \rho_{s,N_0^\beta}^\beta\right] + (1-n_f^\alpha)E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha}^\alpha, \rho_{s,N_0^\beta+1}^\beta\right] \\ &= (n_f^\alpha+n_f^\beta-1)\left\{E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha}^\alpha, \rho_{s,N_0^\beta}^\beta\right] - \sum_\sigma \iint \frac{\rho_{s,f}(\mathbf{r},\mathbf{r}')\rho_{s,N_0^\sigma}^\sigma(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' - \iint \frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\right\} \\ &+ (1-n_f^\beta)\left\{E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha}^\alpha, \rho_{s,N_0^\beta}^\beta\right] - \iint \frac{\rho_{s,f}(\mathbf{r},\mathbf{r}')\rho_{s,N_0^\alpha}^\alpha(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' - \frac{1}{2}\iint \frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\right\} \\ &+ (1-n_f^\alpha)\left\{E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha}^\alpha, \rho_{s,N_0^\beta}^\beta\right] - \iint \frac{\rho_{s,f}(\mathbf{r},\mathbf{r}')\rho_{s,N_0^\beta}^\beta(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' - \frac{1}{2}\iint \frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\right\} \\ &= E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha}^\alpha, \rho_{s,N_0^\beta}^\beta\right] - \sum_\sigma n_f^\sigma \iint \frac{\rho_{s,f}(\mathbf{r},\mathbf{r}')\rho_{s,N_0^\sigma}^\sigma(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' - \frac{1}{2}\sum_\sigma n_f^\sigma \iint \frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \quad \text{[S15]} \end{aligned}$$

for $1 < n_f^\alpha + n_f^\beta \le 2$. Thus, Eqs S14 and S15 are of the same form, which means that there is no derivative discontinuity for the HF exchange energy at fractional spins. The correction from the difference, $\tilde{E}_{\mathrm{X}}^{\mathrm{HF}} - E_{\mathrm{X}}^{\mathrm{HF}}$, is thus formulated as

$$\Delta E_{\mathrm{X}}^{\mathrm{HF}}\left[\rho_{s,N_0^\alpha+n_f^\alpha}^\alpha, \rho_{s,N_0^\beta+n_f^\beta}^\beta\right] = -\frac{(n_f^\alpha - n_f^{\alpha 2}) + (n_f^\beta - n_f^{\beta 2})}{2}\iint \frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \quad \text{[S16]}$$

Different from Eq. S11, Eq. S16 contains only the same-spin contribution, which is the same in magnitude but different in sign as compared to the same-spin contribution of Eq. S11.

C. The correction to exchange density functionals and the global fractional-charge correction. Different from the Coulomb and HF exchange energies, exchange and correlation density functionals are no longer simple quadratic functions of n_f^σ, usually they are all kinds of complicated functions. Therefore, the exact density-functional form of correction is hard to derive and compute, even so we can still derive a simple form that captures most of the exact correction.

The correction to exchange functionals was originally derived in (5). This correction can be obtained by focusing only on the n_f^α and n_f^β fractional electrons, i.e.

$$\Delta E_{\mathrm{X}}\left[\rho^\alpha_{N_0^\alpha+n_f^\alpha},\rho^\beta_{N_0^\beta+n_f^\beta}\right]\approx\Delta E_{\mathrm{X}}\left[n_f^\alpha\rho_f,n_f^\beta\rho_f\right]. \tag{S17}$$

Based on the LDA exchange functional (13), the correction takes the following form:

$$\Delta E_{\mathrm{X}}\left[n_f^\alpha\rho_f,n_f^\beta\rho_f\right]=-[(n_f^\alpha-n_f^{\alpha 2})+(n_f^\beta-n_f^{\beta 2})]\frac{C_{\mathrm{X}}}{3}\int[\rho_f(\mathbf{r})]^{4/3}d\mathbf{r}. \tag{S18}$$

By combining those same-spin contributions from Eqs S11, S16 and S18, we finally arrive at the global fractional-charge (FC) correction

$$\Delta E_{\mathrm{CO}}^{\mathrm{FC}}(N_0^\alpha+n_f^\alpha,N_0^\beta+n_f^\beta)=\frac{1}{2}[(n_f^\alpha-n_f^{\alpha 2})+(n_f^\beta-n_f^{\beta 2})]\kappa^{\mathrm{FC}}[\rho_f], \tag{S19}$$

where κ^{FC} is the FC curvature, defined by

$$\kappa^{\mathrm{FC}}[\rho_f]=(1-d_{\mathrm{X}}^{\mathrm{HF}})\left[\iint\frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'-\frac{2C_{\mathrm{X}}}{3}\int[\rho_f(\mathbf{r})]^{4/3}d\mathbf{r}\right], \tag{S20}$$

$d_{\mathrm{X}}^{\mathrm{HF}}$ is the amount of HF exchange energy in the parent functional. Eq. S19 can be applied to any LDA, GGA, hybrid-GGA, etc.

Actually, the correction of Eq. S19 greatly corrects the FC error, however it enlarges the errors for systems with fractional-spin (FS) states. To further correct the FS error, an effective treatment of the opposite-spin contribution will be introduced in next subsection. Corresponding to the FC correction from the same-spin contribution, all the opposite-spin contribution constitutes the FS correction.

D. The correction to correlation density functionals and the global fractional-spin correction. As the correlation energy is much small and complicated as compared to the exchange energy, thus only the correction to the exchange energy was taken into account in the same-spin correction. Different from the same-spin case, the opposite-spin correction seems much more intractable. As the exchange part provides no contribution to the interaction between electrons of opposite spins, unavoidably the correlation part has to be taken into account for a better correction. Indeed, the correction to the correlation part is so important that its accuracy decides whether the imposed FS correction makes sense or not.

Here the FS correction is formulated as

$$\Delta E_{\mathrm{CO}}^{\mathrm{FS}}(N_0^\alpha+n_f^\alpha,N_0^\beta+n_f^\beta)=-\Lambda(n_f^\alpha,n_f^\beta)\kappa^{\mathrm{FS}}[\rho_f], \tag{S21}$$

where $\Lambda(n_f^\alpha,n_f^\beta)$ is defined in Eq. S12, and κ^{FS} is the FS curvature, which is

$$\kappa^{\mathrm{FS}}[\rho_f]=\iint\frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+\kappa_{\mathrm{C}}[\rho_f]. \tag{S22}$$

The two terms on the rhs of Eq. S22 are curvatures from the Coulomb energy and the correlation functional respectively. Next, a general form of the curvature for the correlation functional, $\kappa_{\mathrm{C}}[\rho_f]$, will be derived.

First approximate correlation functionals can be expressed in form of

$$E_{\mathrm{C}}[\rho,\zeta]=\int\rho(\mathbf{r})\epsilon_{\mathrm{C}}[\rho,\zeta]d\mathbf{r}. \tag{S23}$$

$\epsilon_{\mathrm{C}}[\rho,\zeta]$ is the functional representing correlation energy per electron, which can be formulated as

$$\epsilon_{\mathrm{C}}[\rho,\zeta]=\epsilon_{\mathrm{C}}^0[\rho]+(\epsilon_{\mathrm{C}}^1[\rho]-\epsilon_{\mathrm{C}}^0[\rho])g[\rho,\zeta], \tag{S24}$$

where $\epsilon_{\mathrm{C}}^0[\rho]$ and $\epsilon_{\mathrm{C}}^1[\rho]$ are the spin-compensated and fully spin-polarized correlation energy densities. Eq. S23 is general and makes no local approximation. ρ is the total density, and ζ is the spin polarization parameter, they are obtained as

$$\rho(\mathbf{r})=\rho^\alpha(\mathbf{r})+\rho^\beta(\mathbf{r}),\quad\zeta(\mathbf{r})=\frac{\rho^\alpha(\mathbf{r})-\rho^\beta(\mathbf{r})}{\rho(\mathbf{r})}. \tag{S25}$$

These two quantities are identical to ρ^α and ρ^β when used as basic variables of functionals, therefore any LDA, GGA, etc. can be reformulated in form of Eq. S23.

The functional $g[\rho,\zeta]$ in Eq. S24 serves as a weight factor between the two extreme cases $\zeta = 0$ and $\zeta = 1$ (2). In fact, this functional is the main reason of the FS error in correlation functionals, which can be understood by an example: for a system with the total density unchanged, such as $\mathrm{H}(n^\alpha, n^\beta)$ with constant total electrons (i.e. $n^\alpha + n^\beta = C$), in this case, $\epsilon^0_{\mathrm{C}}[\rho]$ and $\epsilon^1_{\mathrm{C}}[\rho]$ also remain unchanged, therefore $g[\rho,\zeta]$ is the main factor that causes the energy deviation from constant.

To extract those most important nonlinear terms, i.e. the quadratic terms, $g[\rho,\zeta]$ is expanded into Taylor series of ζ,

$$\begin{aligned} g[\rho,\zeta] &= g[\rho,\zeta]|_{\zeta=0} + \frac{\partial g[\rho,\zeta]}{\partial\zeta}\bigg|_{\zeta=0}\zeta + \frac{1}{2!}\frac{\partial^2 g[\rho,\zeta]}{(\partial\zeta)^2}\bigg|_{\zeta=0}\zeta^2 + \cdots \\ &= g^{(0)} + g^{(1)}\zeta + g^{(2)}\zeta^2 + g^{(3)}\zeta^3 + g^{(4)}\zeta^4 + \cdots, \end{aligned} \qquad [\text{S26}]$$

with

$$g^{(n)} = \frac{1}{n!}\frac{\partial^n g[\rho,\zeta]}{(\partial\zeta)^n}\bigg|_{\zeta=0}. \qquad [\text{S27}]$$

Note that the expansion of Eq. S26 does not mean that $g[\rho,\zeta]$ depends only on ζ. To make Eq. S23 a general form of correlation functional, $g[\rho,\zeta]$ should be allowed to depend also on $\nabla\zeta$, $\Delta\zeta$, and so on. For a $g[\rho,\zeta]$ depending on ζ, $\nabla\zeta$, $\Delta\zeta$, etc., we only expand it on ζ, which means that the coefficients $g^{(n)}$ still depend on $\nabla\zeta$, $\Delta\zeta$, etc., this does not affect the derivations below.

There are three conditions that $g[\rho,\zeta]$ should obey,

$$g[\rho,\zeta]|_{\zeta\to 0} = 0, g[\rho,\zeta]|_{\zeta\to 1} = 1, g[\rho,-\zeta] = g[\rho,\zeta]. \qquad [\text{S28}]$$

With these conditions, Eq. S26 reduces to

$$g[\rho,\zeta] = g^{(2)}\zeta^2 + g^{(4)}\zeta^4 + g^{(6)}\zeta^6 + \cdots, \qquad [\text{S29}]$$

with

$$g^{(2)} + g^{(4)} + g^{(6)} + \cdots = 1. \qquad [\text{S30}]$$

Using Eq. S25, we obtain

$$\zeta^2 = 1 - 4\frac{\rho^\alpha\rho^\beta}{\rho^2}. \qquad [\text{S31}]$$

By inserting ζ^2 into Eq. S29, $g[\rho,\zeta]$ can be reformulated as

$$\begin{aligned} g[\rho,\zeta] &= g^{(2)}\left(1 - 4\frac{\rho^\alpha\rho^\beta}{\rho^2}\right) + g^{(4)}\left(1 - 4\frac{\rho^\alpha\rho^\beta}{\rho^2}\right)^2 + g^{(6)}\left(1 - 4\frac{\rho^\alpha\rho^\beta}{\rho^2}\right)^3 + \cdots \\ &= \{g^{(2)} + g^{(4)} + g^{(6)} + \cdots\} - 4\{g^{(2)} + 2g^{(4)} + 3g^{(6)} + \cdots\}\frac{\rho^\alpha\rho^\beta}{\rho^2} + O\Big(\frac{\rho^\alpha\rho^\beta}{\rho^2}\Big)^2 \\ &= 1 - 4\Big\{1 + \sum_{n\geq 2}(n-1)g^{(2n)}\Big\}\frac{\rho^\alpha\rho^\beta}{\rho^2} + O\Big(\frac{\rho^\alpha\rho^\beta}{\rho^2}\Big)^2 \\ &= 1 - 4(1+\eta)\frac{\rho^\alpha\rho^\beta}{\rho^2} + O\Big(\frac{\rho^\alpha\rho^\beta}{\rho^2}\Big)^2, \end{aligned} \qquad [\text{S32}]$$

where

$$\eta = \sum_{n\geq 2}(n-1)g^{(2n)}. \qquad [\text{S33}]$$

Therefore the correlation energy of Eq. S23, can be expanded into

$$E_{\mathrm{C}}[\rho,\zeta] = \int \rho(\mathbf{r})\epsilon^1_{\mathrm{C}}[\rho]d\mathbf{r} - 4\int (1+\eta)(\epsilon^1_{\mathrm{C}}[\rho] - \epsilon^0_{\mathrm{C}}[\rho])\frac{\rho^\alpha(\mathbf{r})\rho^\beta(\mathbf{r})}{\rho(\mathbf{r})}d\mathbf{r} + \int \rho(\mathbf{r})(\epsilon^1_{\mathrm{C}}[\rho] - \epsilon^0_{\mathrm{C}}[\rho])O\Big(\frac{\rho^\alpha(\mathbf{r})\rho^\beta(\mathbf{r})}{\rho(\mathbf{r})^2}\Big)^2 d\mathbf{r}. \qquad [\text{S34}]$$

Similar to Eq. S17, now we focus only on the n^α_f and n^β_f fractional electrons. When $n^\alpha_f + n^\beta_f = 1$, the correlation energy by Eq. S34 is

$$E_{\mathrm{C}}[\rho_f, n^\alpha_f - n^\beta_f] = \int \rho_f(\mathbf{r})\epsilon^1_{\mathrm{C}}[\rho_f]d\mathbf{r} - 4n^\alpha_f n^\beta_f\int (1+\eta)\rho_f(\mathbf{r})(\epsilon^1_{\mathrm{C}}[\rho_f] - \epsilon^0_{\mathrm{C}}[\rho_f])d\mathbf{r} + O(n^\alpha_f n^\beta_f)^2. \qquad [\text{S35}]$$

As we know that the energy of a system with $n^\alpha_f + n^\beta_f = 1$ should be the same as that of the system in normal integer-spin state ($\eta = 1$), thus we obtain the correction

$$\Delta E_{\mathrm{C}}[\rho_f, n^\alpha_f - n^\beta_f] = E_{\mathrm{C}}[\rho_f, 1] - E_{\mathrm{C}}[\rho_f, n^\alpha_f - n^\beta_f] = 4n^\alpha_f n^\beta_f\int (1+\eta)\rho_f(\mathbf{r})(\epsilon^1_{\mathrm{C}}[\rho_f] - \epsilon^0_{\mathrm{C}}[\rho_f])d\mathbf{r}, \qquad [\text{S36}]$$

where we ignore the high order terms, $O(n^\alpha_f n^\beta_f)^2$. Therefore the curvature κ_{C} in Eq. S22 takes the following form:

$$\kappa_{\mathrm{C}}[\rho_f] = -4\int (1+\eta)\rho_f(\mathbf{r})(\epsilon^1_{\mathrm{C}}[\rho_f] - \epsilon^0_{\mathrm{C}}[\rho_f])d\mathbf{r}. \qquad [\text{S37}]$$

η is an unknown functional defined in Eq. S33, whose exact form should be very complicated. Thus instead of deriving the exact form, determining an appropriate constant for η can be already enough to allow a good κ_{C}. Here we use the point, $(n_f^\alpha, n_f^\beta) = (0.5, 0.5)$, to determine η, as the FS error is the largest at this point. The correct correction for this point should be

$$E_{\mathrm{C}}[\rho_f, 1] - E_{\mathrm{C}}[\rho_f, 0] = \int \rho_f(\mathbf{r})\epsilon_{\mathrm{C}}^1[\rho_f]d\mathbf{r} - \int \rho_f(\mathbf{r})\epsilon_{\mathrm{C}}^0[\rho_f]d\mathbf{r}, \qquad \text{[S38]}$$

while the correction from Eq. S36 is

$$\Delta E_{\mathrm{C}}[\rho_f, 0] = \int (1+\eta)\rho_f(\mathbf{r})(\epsilon_{\mathrm{C}}^1[\rho_f] - \epsilon_{\mathrm{C}}^0[\rho_f])d\mathbf{r}. \qquad \text{[S39]}$$

By comparing Eqs. S38 with S39, finally we obtain $\eta = 0$.

The correlation curvature of Eq. S37 is one of the key achievements in this paper. The form is general, which can be applied to any LDA, GGA, etc. by bringing in different kinds of approximated ϵ_{C}^0 and ϵ_{C}^1. Similar to the LDA exchange functional used in the FC curvature, here we would like to use a simple LDA correlation functional developed recently (14). ϵ_{C}^0 and ϵ_{C}^1 are approximated by form

$$\epsilon_{\mathrm{C}}[\rho] = a\ln\big(1 + \frac{b}{r_s} + \frac{b}{r_s^2}\big), \qquad \text{[S40]}$$

where $r_s = (4\pi\rho/3)^{-1/3}$, and a and b are two parameters determined by the high-density limit, they are

$$a = \frac{\ln 2 - 1}{2\pi^2}; b = 20.4562557, \qquad \text{[S41]}$$

for ϵ_{C}^0, and

$$a = \frac{\ln 2 - 1}{4\pi^2}; b = 27.4203609, \qquad \text{[S42]}$$

for ϵ_{C}^1.

2. Fractional-Spin Localized Orbital Scaling Correction (FSLOSC)

A. Orbital localization. Localized orbitals (LOs, $\{\phi_p\}$) used in this paper are obtained by unitary transformation upon COs ($\{\varphi_p\}$) (15),

$$\phi_p(\mathbf{r}) = \sum_q U_{pq}\varphi_q(\mathbf{r}). \qquad \text{[S43]}$$

And the occupation

$$\lambda_{pq}^\sigma = \langle\phi_p|\rho_s^\sigma|\phi_q\rangle, \qquad \text{[S44]}$$

is now a matrix. For this occupation matrix, diagonal elements represent the occupations of LOs, which obey $\sum_p \lambda_{pp}^\sigma = N^\sigma$.

Here we want to make clear the meaning of off-diagonal elements, λ_{pq}^σ, as they play a special role in the construction of FS correction. Each off-diagonal element connects to a LO pair, with the magnitude equal to $\sum_i^{occ.}\langle\phi_p|\varphi_i\rangle\langle\varphi_i|\phi_q\rangle$, which represents how much the pair of LOs formed from the mixing of the same occupied COs.

The LOs keep the density matrix intact via

$$\rho_s^\sigma = \sum_{pq}|\phi_p\rangle\lambda_{pq}^\sigma\langle\phi_q|. \qquad \text{[S45]}$$

The unitary matrix U is obtained through the minimization of the following objective function,

$$\begin{aligned} F[\mathrm{U}, \{\varphi_p\}, \{\varepsilon_p\}] &= \sum_p \Big[\langle\phi_p|\mathbf{r}^2|\phi_p\rangle - \langle\phi_p|\mathbf{r}|\phi_p\rangle^2\Big] + \sum_{pq}\omega_{pq}|\langle\phi_p|\varphi_q\rangle|^2 \\ &= \sum_p \Big[\sum_{rs} U_{pr}U_{ps}\langle\varphi_r|\mathbf{r}^2|\varphi_s\rangle - \Big(\sum_{rs} U_{pr}U_{ps}\langle\varphi_r|\mathbf{r}|\varphi_s\rangle\Big)^2\Big] + \sum_{pq}\omega_{pq}U_{pq}^2, \end{aligned} \qquad \text{[S46]}$$

where the first term on the rhs is just the objective function of Foster-Boys localization (16), while the second term is brought in to restrict the mixing of different COs.

To increase the ability of capturing the delocalized nature of reaction transition states, in this work we use a modified ω_{pq} of the form

$$\omega_{pq} = R_0^2\{\exp[|\varepsilon_p - \varepsilon_q|/\varepsilon_0 + \mathrm{erfc}(\eta\sqrt{d_p d_q})] - 1\}, \qquad \text{[S47]}$$

where ε_p is the p-th CO energy; d_p is used to reflect the delocalization of the p-th CO, so it is called orbital delocalization factor. Here orbital delocalization factor takes the form of

$$d_p = \sum_{A<B} Q_p(A)|\mathbf{R}_A - \mathbf{R}_B|Q_p(B), \qquad \text{[S48]}$$

where $\mathbf{R}_A$ is the position of atom A, and $Q_p(A)$ represents how much the p-th CO localized on atom A, which can be obtained from (similar to Mulliken population analysis (17))

$$Q_p(A) = \sum_{\mu(\in A)} \sum_{\nu} P^p_{\mu\nu} S_{\nu\mu}. \qquad [S49]$$

Here μ and ν are atomic orbital indices, $P^p_{\mu\nu}$ is the density matrix of the p-th CO.

The larger the value of ω_{pq}, the smaller the mixing of the p-th and q-th orbitals. Thus it is understandable to set the diagonal elements, ω_{pp}, to 0, which allows the p-th LO to retain the more component of the p-th CO. With this ω_{pq}, the mix between COs whose energies are far apart is suppressed. Thus core occupied and high unoccupied COs, as their energies are of much greater magnitude as compared to that of frontier orbitals (those orbitals around HOMO and LUMO), can not mix with unoccupied and occupied COs respectively, and the corresponding blocks of the occupation matrix remain diagonal, with the diagonal elements equal to 1 (0). Only frontier orbitals, as the energies of occupied and unoccupied orbitals are relatively close to each other, are possible to mix together to form fractionally occupied LOs. It means that if we only need the total electronic energy or frontier orbital energies, then core occupied and high unoccupied COs can be excluded from the localization and subsequent procedures to make the computational cost of the FC and FS corrections much smaller than the SCF calculation of common density functional approximations (DFAs). Besides more delocalized COs (with larger orbital delocalization factors) are more likely to mix with each other to form LOs, which provides a way to characterize reaction transition states because the COs of transition states are more delocalized as compared to those of equilibrium geometries. For atoms, as the orbital delocalization factors of all COs are equal to zero, it is hard for the COs to mix each other.

It should be noted that, in order to capture local FS information for FS correction, spin restriction is imposed during localization. It means that we only have to optimized one set of LOs, which can be occupied by both alpha and beta electrons. Besides, in the self-consistent calculation of FS correction, the COs and CO energies used in the localization procedure are from the projection and diagonalization of $(h^{\mathrm{DFA},\alpha} + h^{\mathrm{DFA},\beta})/2$ in closed, open, and virtual orbital spaces.

B. Fractional-charge correction. With the LOs and the occupation matrix, The FC correction (15) is constructed as

$$\Delta E^{\mathrm{FC}}_{\mathrm{LO}} = \sum_p \sum_\sigma \frac{1}{2}(\lambda^\sigma_{pp} - \lambda^{\sigma 2}_{pp})\kappa^{\mathrm{FC}}[\rho_p, \rho_p] - \sum_{p\neq q} \sum_\sigma \frac{1}{2}\lambda^{\sigma 2}_{pq}\kappa^{\mathrm{FC}}[\rho_p, \rho_q], \qquad [S50]$$

where the FC curvature $\kappa^{\mathrm{FC}}[\rho_p, \rho_q]$ is defined by

$$\kappa^{\mathrm{FC}}[\rho_p, \rho_q] = \iint \frac{\rho_p(\mathbf{r})\rho_q(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \frac{2C_{\mathrm{X}}}{3} \int [\rho_p(\mathbf{r})\rho_q(\mathbf{r})]^{2/3} d\mathbf{r}. \qquad [S51]$$

This curvature should be multiplied by $1 - d^{\mathrm{HF}}_{\mathrm{X}}$ for a hybrid parent functional. Here $\rho_p(\mathbf{r}) = |\phi_p(\mathbf{r})|^2$ is the density of the p-th LO.

The first term on the rhs of Eq. S50 is directly generalized from Eq. S19, except that it encompasses the summation over all the fractionally occupied LOs. The second term is brought in to dispel the unwanted interactions between LO pairs. For example, in the case of H_2^+ dissociation, as the H-H bond stretched out, the first two COs would gradually become degenerate and more and more delocalized, which compels them to mix each other and form two LOs located at these two H atoms respectively. As there is only one alpha electron for this systems, the elements of the occupation matrix can be easily obtained from

$$\lambda^\alpha_{pq} = \langle\phi_p|\varphi_1\rangle\langle\varphi_1|\phi_q\rangle = U_{p1}U_{q1}, \qquad [S52]$$

and they obey

$$\lambda^{\alpha 2}_{12} = \lambda^{\alpha 2}_{21} = (U_{11}U_{21})^2 = U^2_{11}U^2_{21} = \lambda^\alpha_{11}\lambda^\alpha_{22}. \qquad [S53]$$

Therefore, at dissociation limit, the second term of Eq. S50 reduces to $-\lambda^\alpha_{11}\lambda^\alpha_{22}\iint \frac{\rho_1(\mathbf{r})\rho_2(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'$, which removes the unphysical Coulomb interaction between these two LOs.

C. Fractional-spin correction for well-separated LOs. Similarly, the global FS correction of Eq. S21 can be generalized to

$$\Delta E^{\mathrm{FS}'}_{\mathrm{LO}} = -\sum_p \Lambda(\lambda^\alpha_{pp}, \lambda^\beta_{pp})\kappa^{\mathrm{FS}}[\rho_p, \rho_p] + \sum_{p\neq q} \lambda^\alpha_{pq}\lambda^\beta_{pq}\kappa^{\mathrm{FS}}[\rho_p, \rho_q]. \qquad [S54]$$

Here $\Lambda(\lambda^\alpha_{pp}, \lambda^\beta_{pp})$ is defined in Eq. S12, and the FS curvature is

$$\kappa^{\mathrm{FS}}[\rho_p, \rho_q] = \iint \frac{\rho_p(\mathbf{r})\rho_q(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \kappa_{\mathrm{C}}[\sqrt{\rho_p\rho_q}], \qquad [S55]$$

with κ_{C} defined by Eq. S37. The first term on the rhs of Eq. S54 is directly generalized from Eq. S21, which restores the flat-plane behavior for each fragments with fractional spins. The second term corrects the erroneous long-range interaction between fragments caused by the second term on the rhs of Eq. S50. Taking H_2 as example, at dissociation limit, the total densities on both H atoms and the Coulomb interaction between the two fragments are actually good. However the second term in the FC correction (Eq. S50) destroys this correct long-range interaction. With the second term of Eq. S54, the incorrect correction from the FC part can be canceled out. Besides, for those cases with fractional charges but no fractional spins, such as H_2^+ dissociation, the second term of Eq. S54 disappears, that is what we want because the FC correction already has correct long-range interaction for this case.

D. Fractional-spin correction for overlapping LOs. Eq. S54 repairs the dissociation limits for commonly used DFAs, however it is still not enough for the whole potential energy curves of dissociation, actually there would be a huge bump in the curves.

Taking H_2 as example, as the H-H bond stretched out, the only occupied CO will mix with LUMO to form two LOs. These two LOs center on the two H atoms respectively, and their occupations obey

$$\lambda_{ii}^{\alpha} = \lambda_{ii}^{\beta}, \tag{S56}$$

and

$$\begin{cases} \lambda_{11}^{\sigma} = 1-\delta \\ \lambda_{22}^{\sigma} = \delta, \qquad \sigma = \alpha, \beta, \end{cases} \tag{S57}$$

where the value of δ, first equal to 0, increases as the H-H distance gets larger, finally it approaches 0.5 as the two H atoms go far away from each other. Fig. S1 depicts how the LO densities and LO occupations change along H-H bond dissociation.

Here we focus on the Coulomb interaction, as the corrections of this part are normally the largest. Since the spin densities and total density obey the spacial symmetry, even though there are fractional alpha and beta electrons on each H atom, the total number of electrons on each H atom is correct (equal to 1). Therefore, as the H-H bond stretched out from equilibrium, the Coulomb interaction calculated by commonly used DFT methods is actually quite good. However the corrections to the Coulomb interaction from both the first terms of Eqs. S50 and S54 are

$$\delta(1-\delta)\iint \frac{\rho_1(\mathbf{r})\rho_1(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \delta(1-\delta)\iint \frac{\rho_2(\mathbf{r})\rho_2(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \tag{S58}$$

and

$$-\delta^2\iint \frac{\rho_1(\mathbf{r})\rho_1(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' - \delta^2\iint \frac{\rho_2(\mathbf{r})\rho_2(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \tag{S59}$$

respectively. Here the second terms from both Eqs. S50 and S54 are ignored, as they cancel each other. When δ is small, the positive correction of Eq. S58 can not be completely cancelled out by the negative correction of Eq. S59, resulting in a positive overall correction which further worsens the already-too-high energy from mainstream DFAs. Only when δ approaches 0.5, these two corrections cancel each other. This accounts for the good dissociation limit but a bump in the dissociation energy curve.

Now we know that a bump comes out because the large positive FC correction can not be compensated properly by the FS correction of Eq. S54. It happens in the region where an occupied CO begins to split into two overlapping LOs with fractional occupations. To fix this, another correction is proposed for this region, which takes the form of

$$\Delta E_{\mathrm{LO}}^{\mathrm{FS}''} = -\sum_{p}\Gamma(\lambda_{pp}^{\alpha}, \lambda_{pp}^{\beta})\kappa^{\mathrm{FS}}[\rho_p, \rho_p], \tag{S60}$$

with

$$\Gamma(\lambda_{pp}^{\alpha}, \lambda_{pp}^{\beta}) = \min(\lambda_{pp}^{\alpha}, \lambda_{pp}^{\beta})\min(1-\lambda_{pp}^{\alpha}, 1-\lambda_{pp}^{\beta}). \tag{S61}$$

For H_2 dissociation, $\Gamma(\lambda_{11}^{\alpha}, \lambda_{11}^{\beta}) = \Gamma(\lambda_{22}^{\alpha}, \lambda_{22}^{\beta}) = \delta(1-\delta)$. Thus this correction can properly compensate the large positive correction from Eq. S58. Besides, for any LO, Eq. S61 is nonzero only when the alpha and beta occupations are both fractional, therefore this correction takes effect only for FS problems. In addition, Eq. S60 should be multiplied by $1-d_{\mathrm{X}}^{\mathrm{HF}}$ for a hybrid parent functional, which is similar to the FC correction for a hybrid functional.

E. Final fractional-spin correction. By combining the FS corrections for both well-separated and overlapping LOs, the final FS correction is formulated as

$$\Delta E_{\mathrm{LO}}^{\mathrm{FS}} = -\sum_{p}\left[(1-S_p)\Lambda(\lambda_{pp}^{\alpha}, \lambda_{pp}^{\beta}) + S_p\Gamma(\lambda_{pp}^{\alpha}, \lambda_{pp}^{\beta})\right]\kappa^{\mathrm{FS}}[\rho_p, \rho_p] + \sum_{p\neq q}\lambda_{pq}^{\alpha}\lambda_{pq}^{\beta}\kappa^{\mathrm{FS}}[\rho_p, \rho_q], \tag{S62}$$

with

$$S_p = \mathrm{erf}\left(\gamma\left(\int\sqrt{\rho_p(\mathbf{r})\rho_{q_{pmax}}(\mathbf{r})}d\mathbf{r}\right)^{\frac{1}{2}}\right), \tag{S63}$$

where the q_{pmax} can be obtained via $\mathrm{argmax}_q(\lambda_{pq}^{\alpha 2} + \lambda_{pq}^{\beta 2})$. Fig. S2 illustrates how S_p changes along H-H bond dissociation. S_p is designed to become zero when the p-th and q_{pmax}-th LOs are well-separated, so that the correction of the p-th LO is degraded to $-\Lambda(\lambda_{pp}^{\alpha}, \lambda_{pp}^{\beta})\kappa^{\mathrm{FS}}[\rho_p, \rho_p]$, indicating that the flat-plane condition has been imposed. When the LO pair are close to each other, S_p is large, so the correction for overlapping LOs is turned on. Besides, since core occupied (high unoccupied) COs cannot mix with unoccupied (occupied) COs to form fractionally occupied LOs, and the COs of atoms (with the orbital delocalization factors equal to zero) rarely mix with each other, which makes the $(\lambda_{pq_{pmax}}^{\alpha 2} + \lambda_{pq_{pmax}}^{\beta 2})$ quite small and the q_{pmax} found meaningless, therefore we set S_q to zero when $(\lambda_{pq_{pmax}}^{\alpha 2} + \lambda_{pq_{pmax}}^{\beta 2})$ is almost zero. Due to $\Gamma(\lambda_{pp}^{\alpha}, \lambda_{pp}^{\beta})$ and $\Lambda(\lambda_{pp}^{\alpha}, \lambda_{pp}^{\beta})$, this FS correction is derivative discontinuous.

F. Orbital energies of FSLOSC. With both FC and FS corrections, the total energy is now formulated as

$$E_{\mathrm{Tot}}^{\mathrm{FSLOSC}} = E^{\mathrm{DFA}} + \Delta E_{\mathrm{LO}}^{\mathrm{FC}} + \Delta E_{\mathrm{LO}}^{\mathrm{FS}}. \tag{S64}$$

The orbital energies can be calculated by

$$\begin{aligned}\varepsilon_s^{\mathrm{FSLOSC},\sigma} = \frac{\partial E_{\mathrm{Tot}}^{\mathrm{FSLOSC}}}{\partial n_s^\sigma} &= \langle\varphi_s|\frac{\delta E_{\mathrm{Tot}}^{\mathrm{FSLOSC}}}{\delta\rho_s^\sigma}|\varphi_s\rangle = \langle\varphi_s|h^{\mathrm{FSLOSC},\sigma}|\varphi_s\rangle \\ &= \langle\varphi_s|h^{\mathrm{DFA},\sigma} + \Delta h^{\mathrm{FC},\sigma} + \Delta h^{\mathrm{FS},\sigma}|\varphi_s\rangle.\end{aligned} \tag{S65}$$

Here the FSLOSC effective Hamiltonian includes three parts, they are $h^{\mathrm{DFA},\sigma}$ from the parent DFA, $\Delta h^{\mathrm{FC},\sigma}$ from the FC correction, and $\Delta h^{\mathrm{FS},\sigma}$ from the FS correction. Using frozen-orbital assumption in post-SCF calculations or ignoring the dependence of U matrix on orbitals in self-consistent calculations, $\Delta h^{\mathrm{FC},\sigma}$ and $\Delta h^{\mathrm{FS},\sigma}$ are derived. $\Delta h^{\mathrm{FC},\sigma}$ is

$$\Delta h^{\mathrm{FC},\sigma} \approx \sum_p \big(\frac{1}{2} - \lambda_{pp}^\sigma\big)\kappa^{\mathrm{FC}}[\rho_p,\rho_p]|\phi_p\rangle\langle\phi_p| - \sum_{p\neq q}\lambda_{pq}^\sigma\kappa^{\mathrm{FC}}[\rho_p,\rho_q]|\phi_p\rangle\langle\phi_q|. \tag{S66}$$

By contrast, the derivation of $\Delta h^{\mathrm{FS},\sigma}$ requires extra consideration, as the FS correction is derivative discontinuous, where $\Gamma(\lambda_{pp}^\alpha,\lambda_{pp}^\beta)$ is non-differentiable when $\lambda_{pp}^\alpha = \lambda_{pp}^\beta$, and $\Lambda(\lambda_{pp}^\alpha,\lambda_{pp}^\beta)$ is non-differentiable when $\lambda_{pp}^\alpha + \lambda_{pp}^\beta = 1$. Therefore, when deriving $\frac{\partial E_{\mathrm{LO}}^{\mathrm{FS}}}{\partial n_s^\sigma}$, left or right derivative should be determined for $\Gamma(\lambda_{pp}^\alpha,\lambda_{pp}^\beta)$ and $\Lambda(\lambda_{pp}^\alpha,\lambda_{pp}^\beta)$. Inspired by the orbital energy calculations of normal DFAs: $\lim_{\Delta n_i^\sigma\to 0}\frac{E_{\mathrm{Tot}}^{\mathrm{DFA}}(N)-E_{\mathrm{Tot}}^{\mathrm{DFA}}(N-\Delta n_i^\sigma)}{\Delta n_i^\sigma}$ and $\lim_{\Delta n_a^\sigma\to 0}\frac{E_{\mathrm{Tot}}^{\mathrm{DFA}}(N+\Delta n_a^\sigma)-E_{\mathrm{Tot}}^{\mathrm{DFA}}(N)}{\Delta n_a^\sigma}$ are used respectively for energies of occupied and unoccupied COs, here when we calculate the derivatives of $\Gamma(\lambda_{pp}^\alpha,\lambda_{pp}^\beta)$ and $\Lambda(\lambda_{pp}^\alpha,\lambda_{pp}^\beta)$ with respect to λ_{pp}^σ, left derivatives are used for $\lambda_{pp}^\sigma \geq 0.5$ while right derivatives are used for $\lambda_{pp}^\sigma < 0.5$. Therefore, we obtain

$$\frac{\partial\Gamma(\lambda_{pp}^\alpha,\lambda_{pp}^\beta)}{\partial\lambda_{pp}^\alpha} = \begin{cases}1-\lambda_{pp}^\beta, & \lambda_{pp}^\alpha < \lambda_{pp}^\beta \;\;\|\;\; \lambda_{pp}^\alpha = \lambda_{pp}^\beta \;\&\; \lambda_{pp}^\alpha \geq 0.5\\ -\lambda_{pp}^\beta, & \lambda_{pp}^\alpha > \lambda_{pp}^\beta \;\;\|\;\; \lambda_{pp}^\alpha = \lambda_{pp}^\beta \;\&\; \lambda_{pp}^\alpha < 0.5,\end{cases} \tag{S67}$$

and

$$\frac{\partial\Lambda(\lambda_{pp}^\alpha,\lambda_{pp}^\beta)}{\partial\lambda_{pp}^\alpha} = \begin{cases}\lambda_{pp}^\beta, & \lambda_{pp}^\alpha + \lambda_{pp}^\beta < 1 \;\;\|\;\; \lambda_{pp}^\alpha + \lambda_{pp}^\beta = 1 \;\&\; \lambda_{pp}^\alpha \geq 0.5\\ -(1-\lambda_{pp}^\beta), & \lambda_{pp}^\alpha + \lambda_{pp}^\beta > 1 \;\;\|\;\; \lambda_{pp}^\alpha + \lambda_{pp}^\beta = 1 \;\&\; \lambda_{pp}^\alpha < 0.5.\end{cases} \tag{S68}$$

With this, the effective Hamiltonian from the FS correction is

$$\begin{aligned}\Delta h^{\mathrm{FS},\alpha} \approx &-\sum_p \Big[(1-S_p)\frac{\partial\Lambda(\lambda_{pp}^\alpha,\lambda_{pp}^\beta)}{\partial\lambda_{pp}^\alpha} + S_p\frac{\partial\Gamma(\lambda_{pp}^\alpha,\lambda_{pp}^\beta)}{\partial\lambda_{pp}^\alpha}\Big]\kappa^{\mathrm{FS}}[\rho_p,\rho_p]|\phi_p\rangle\langle\phi_p| \\ &+\sum_{p\neq q}\lambda_{pq}^\beta\kappa^{\mathrm{FS}}[\rho_p,\rho_q]|\phi_p\rangle\langle\phi_q|.\end{aligned} \tag{S69}$$

Similarly, $\Delta h^{\mathrm{FS},\beta}$ can be derived.

G. Self-consistent FSLOSC (scFSLOSC). The FSLOSC derived above can be applied as a general approach to existing DFAs, such as LDAs, GGAs, and hybrid GGAs. There are two ways to implement the FSLOSC calculation. One is post-SCF calculation, after the restricted SCF calculation of the parent functional, the COs and CO energies are used to do orbital localization, and then calculate the FSLOSC total energy by Eq. S64 and orbital energies by Eq. S65.

The other one is self-consistent calculation of FSLOSC, i.e. scFSLOSC. With the FSLOSC effective Hamiltonian derived in previous subsection, one can follow the routine restricted SCF calculation or use some gradient optimization algorithm to obtain a set of optimized orbitals and density, based on which the FSLOSC energy is subsequently calculated. As mentioned above, the effective Hamiltonian in previous subsection is derived based on the frozen-orbital assumption, thus we prefer the gradient algorithm together with line search for better convergence.

3. Supplemental test results.

In the main text, only the results of BLYP (18, 19) and (sc)FSLOSC-BLYP are shown. Here more test results of FSLOSC based on LDA (13, 20) and B3LYP (21, 22) are provided.

In this work, all the calculations of DFT and post-HF wave-function methods are based on restricted SCF for both close-shell and open-shell systems. DFT calculations were performed using an in-house developed QM^{4}D program (23), while coupled cluster calculations using Gaussian09 program (24), and MCSCF calculations using NWChem program (25). The basis sets used are 6-311++G(3df, 3pd) (26–28) for HTBH38/08, NHTBH38/08 (29, 30), and G2-97 test sets (31); cc-pVTZ (32) for flat-plane tests (H and Li atoms), H_2^+, H_2, C_2H_6, C_2H_4, C_2, N_2, P_2 and CO; 6-31G(d, p) (33, 34) for HF, 6-31G for NH_3 and H_8; and crenbl basis set (35) for C_{60}. For FSLOSC calculation, only those COs with energies range from -30 to 10 eV are taken into account for orbital localization and subsequent procedures, which makes the computational cost of the FC and FS corrections much smaller than that of calculating SCF-converged COs.

Tab. S1 shows the overall performance of DFAs and FSLOSC-DFAs on predicting barrier heights. The test is based on hydrogen transfer barrier heights (HTBH38/08) and non-hydrogen transfer barrier heights (NHTBH38/08), both these two test sets include 19 reactions with both forward and reverse reaction barrier heights. For this test, FSLOSC-DFAs show obvious improvement over their parent DFAs.

Tab. S2 shows the overall performance of DFAs and FSLOSC-DFAs on thermochemistry, the atomization energies exclusive of the zero-point energies are examined. The G2-97 test set is used, which includes five subsets: G2-1, non-hydrogen, hydrocarbon, substituted hydrocarbon, inorganic hydrides and radicals. For this test, FSLOSC-DFAs show comparable results to their parent DFAs.

Fig. S3 shows the performance of FSLOSC-LDA on energies of H and Li atoms with fractional charges and fractional spins. As is well known that the exact energies should show two flat planes intersecting at $n_\alpha + n_\beta = 1$ for H atom. Commonly used DFAs, such as LDA and BLYP, show great deviation from the flat planes. FSLOSC-LDA displays nearly flat-plane behavior. Besides, this good performance is maintained for the Li atom, which indicates that the FS correction generally corrects the FS errors in commonly used DFAs.

Fig. S4 compares the calculated $-\epsilon_{\mathrm{HOMO}}$ ($-\epsilon_{\mathrm{LUMO}}$) with reference vertical ionization potentials I_{ve} (vertical electron affinities A_{ve}). The CCSD(T) calculations and extrapolated to infinite basis limit are used to obtain the reference data. The testing molecules are from the G2-97 set, where $H_2S(^2A_1)$, $N_2(^2\Pi_u)$, C_6H_6, C_7H_8, H_6C_6O and H_7C_6O are exclusive from the ϵ_{HOMO} or I_{ve} calculations. LDA shows mean absolute deviations (MADs) of 4.29 and 3.85 eV from reference I_{ve} and A_{ve} respectively, the deviations are greatly reduced by FSLOSC-LDA, whose MADs are 0.53 and 0.85 eV.

Figs. S5-S8 show the performance of FSLOSC-DFAs on predicting potential energy curves of systems with strong correlation. FSLOSC-DFAs not only show nice potential energy curves for dissociations of the cationic system H_2^+ (Fig. S5(a)), single-bond systems H_2 (Fig. S5(b)) and H_3C-CH_3 (Fig. S5(c)), but also for double-bond twisted in C_2H_4 (Fig. S5(d)), multiple-bond dissociations of C_2 (both $X^1\Sigma_{\mathrm{g}}^+$ and $B^1\Delta_{\mathrm{g}}$), N_2, and P_2 (Fig. S6). For the cases of heteroatom molecules, Fig. S7 shows that LDA and BLYP give incorrect charge distribution for the dissociation of both single-bond HF and multiple-bond CO, which results in fractionally charged fragments at large interatomic distance. That is why FSLOSC-DFAs based on the densities of commonly used DFAs do not improve the dissociation limits. With the SCF calculations of FSLOSC-DFAs, i.e. scFSLOSC-DFAs, the charges as well as the energies at dissociation limits are corrected. Fig. S8 shows other difficult cases for DFT methods, namely, the simultaneous dissociation of one, two, three N-H bonds in NH_3, and the process of pulling apart eight H atoms in a cubic H_8. scFSLOSC-DFAs also improves greatly the behaviors of DFAs. Note that the dissociation limits still have some deviations, especially for H_8 , since the FS curvature is not perfect for H atom; see Fig. S9.

The success of (sc)FSLOSC-DFAs for these cases indicates the robustness of the FS correction, it provides a viable scheme to rescue the failure of mainstream DFAs for strong correlation.

Table S1. Mean absolute deviations(MADs, in kcal/mol) computed on the HTBH38/08 and NHTBH38/08 test sets for reaction barriers^a.

	LDA	FSLOSC-LDA	BLYP	FSLOSC-BLYP	B3LYP	FSLOSC-B3LYP
HTBH38/08	17.58	13.87	7.37	5.23	3.55	2.33
NHTBH38/08	12.34	7.95	8.28	5.82	4.04	2.92
mean	14.96	10.91	7.83	5.53	3.80	2.63

^{a}HTBH: Hydrogen Transfer Barrier Heights; NHTBH: Non-Hydrogen Transfer Barrier Heights. Geometries and experimental data are from refs. (29, 30)

Table S2. Mean absolute deviations(MADs, in kcal/mol) computed on the G2-97 test set for atomization energies^a.

	LDA	FSLOSC-LDA	BLYP	FSLOSC-BLYP	B3LYP	FSLOSC-B3LYP
G2-1(55)	36.05	35.58	5.57	5.84	2.77	3.58
Non-hydrogen(21)	91.93	92.02	15.30	16.28	5.93	6.50
Hydrocarbons(17)	143.54	142.43	7.12	8.14	1.73	2.03
Substituted Hydrocarbons(42)	121.49	120.68	6.64	6.89	3.14	2.50
Inorganic hydrides and radicals(13)	74.10	72.66	5.65	6.26	3.50	2.71
mean(148)	83.91	83.26	7.44	7.92	3.27	3.43

^{a} Geometries and experimental data are from ref. (31)

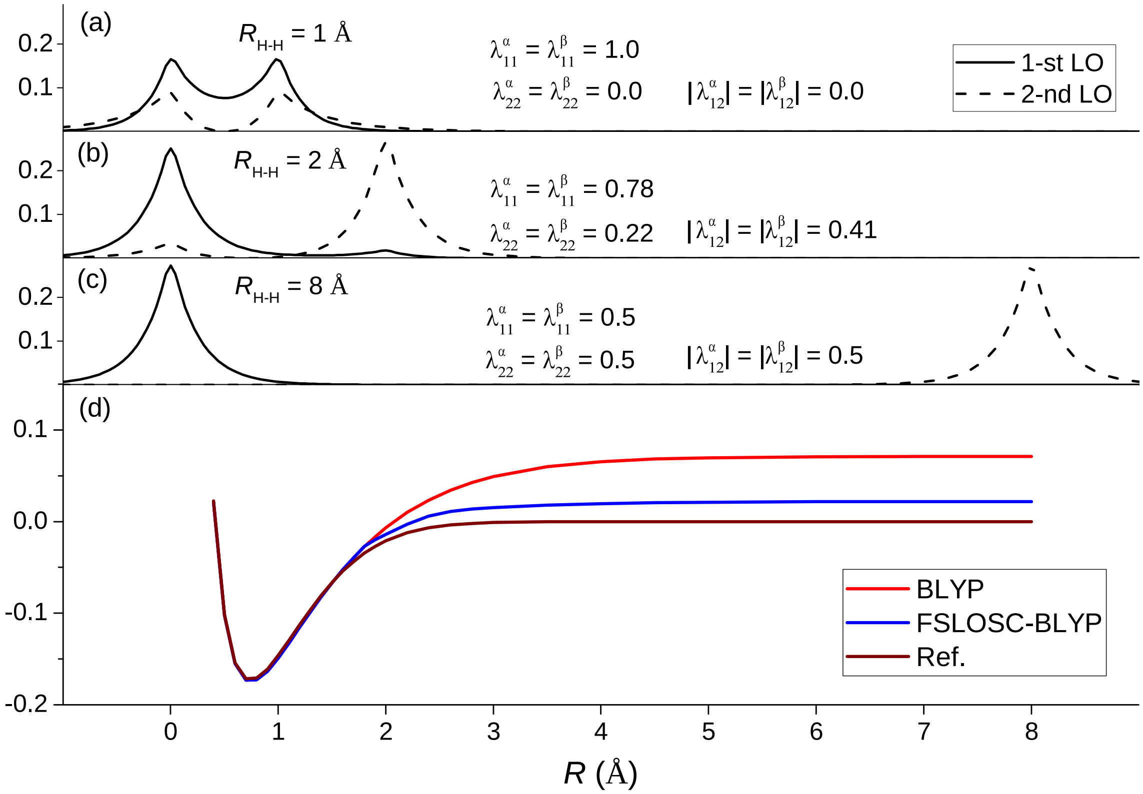

Fig. S1. LO densities plotted along the bonding axis of H_2 at the internuclear distance of (a) $R_{\mathrm{H-H}} = 1\text{Å}$, (b) $R_{\mathrm{H-H}} = 2\text{Å}$, and (c) $R_{\mathrm{H-H}} = 8\text{Å}$. The two H atoms locate at $x = 0$ and $x = R_{\mathrm{H-H}}$ respectively. (c) Potential energy curves for H_2 bond dissociation. The total energy of two doublet H atoms are set to zero. All densities and energies are in a.u.

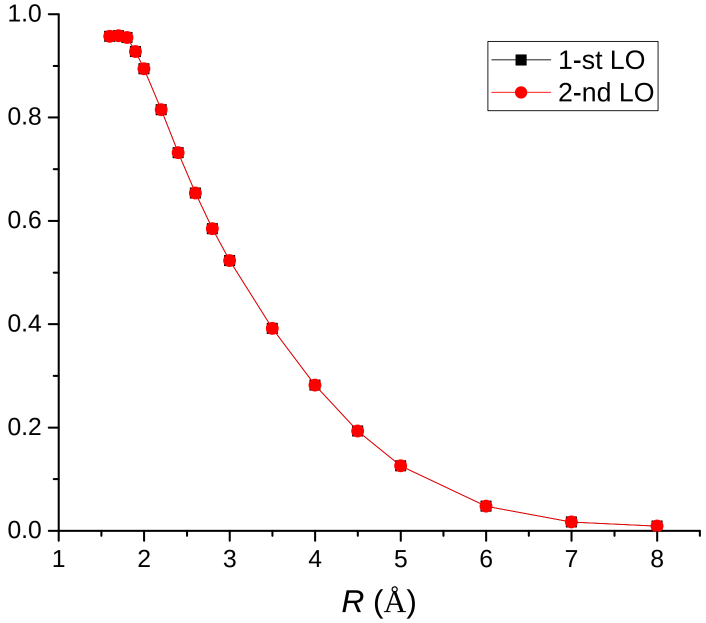

Fig. S2. S_p of Eq. S63 plotted as a function of H-H bond distance for H_2 dissociation. The first two localized orbitals are examined.

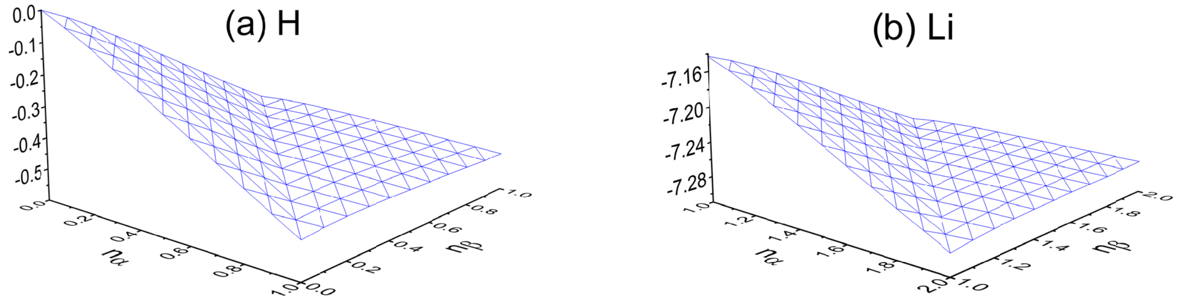

Fig. S3. Energies computed by FSLOSC-LDA for (a) H and (b) Li atoms with fractional charges and fractional spins. All energies are in a.u.

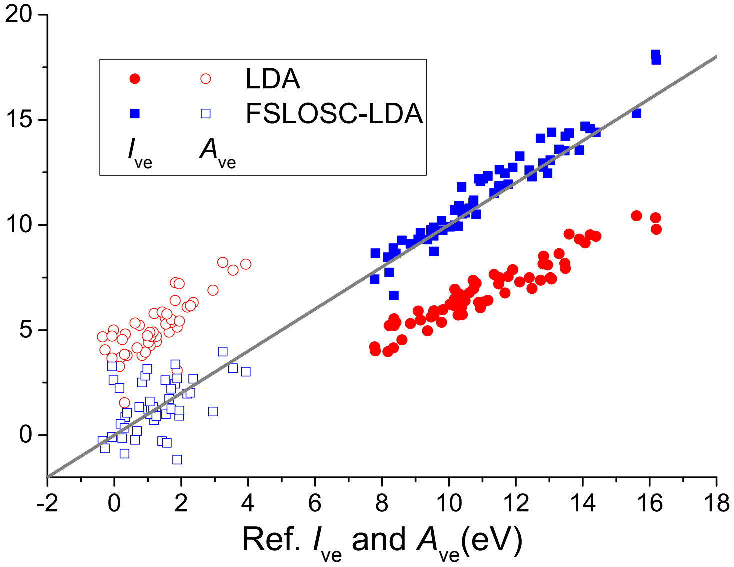

Fig. S4. Calculated $-\epsilon_{\mathrm{HOMO}}$ $(-\epsilon_{\mathrm{LUMO}})$ versus reference I_{ve} (A_{ve}) for 64 (47) molecules from G2-97 set. The solid line indicates $-\epsilon_{\mathrm{HOMO}} = I_{\mathrm{ve}}$ or $-\epsilon_{\mathrm{LUMO}} = A_{\mathrm{ve}}$. All data are in eV.

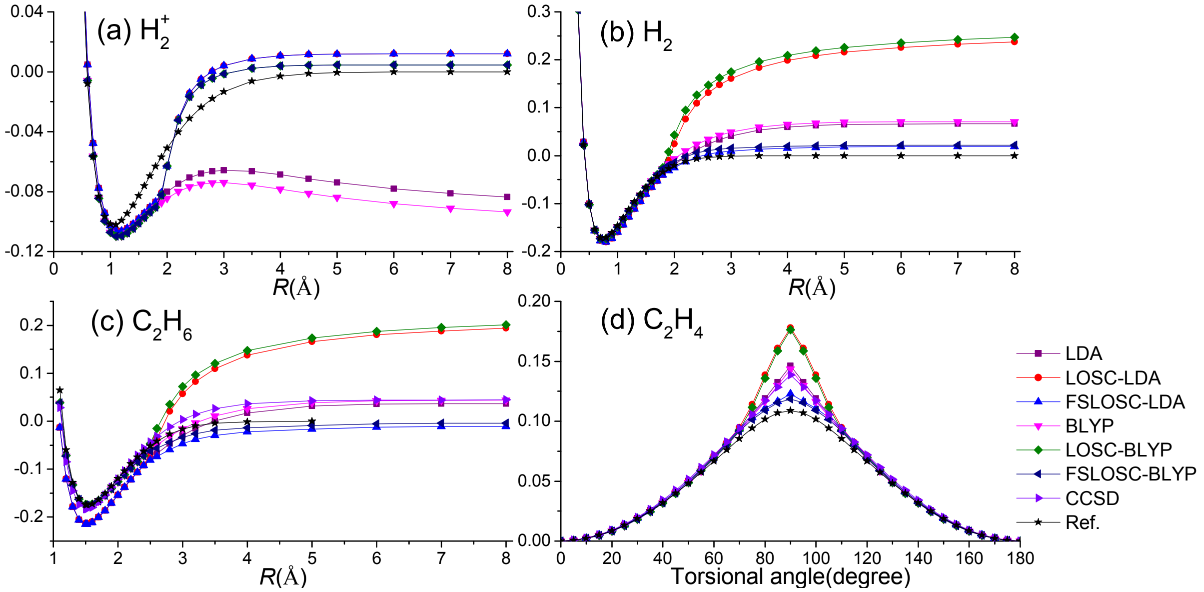

Fig. S5. Potential energy curves for H-H bond dissociation in (a) H_2^+ and (b) H_2, C-C bond dissociation in (c) C_2H_6, and C=C double bond twisted in (d) C_2H_4. The total energies of a doublet H atom, two doublet H atoms, two doublet $\cdot CH_3$ fragments, and C_2H_4 with HCCH torsion angle at $\theta = 0$ are set to zero for H_2^+, H_2, C_2H_6, and C_2H_4 respectively. The reference results are HF for H_2^+, CCSD for H_2, MRCI+Q for C_2H_6, and MR-ccCA for C_2H_4. Reference energies and geometries are from refs. (36) and (37) for C_2H_6 and C_2H_4 respectively. All energies are in a.u.

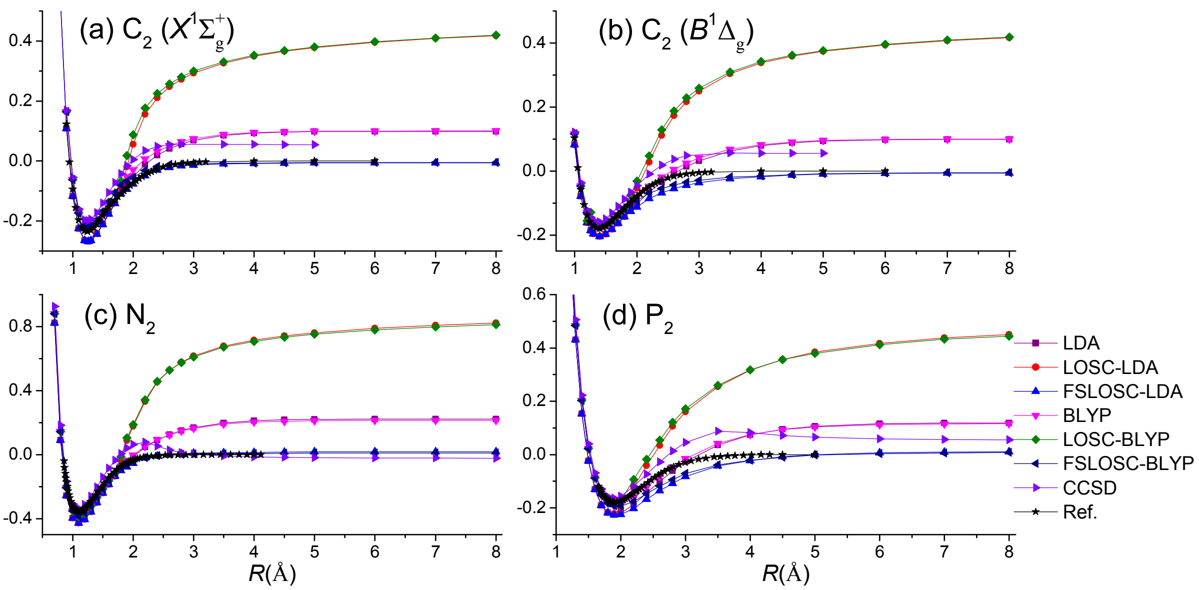

Fig. S6. Potential energy curves for C-C multiple-bond dissociation in C$_2$ (two singlet states (a) $X^1\Sigma_\mathrm{g}^+$ and (b) $B^1\Delta_\mathrm{g}$ are calculated, the ground state is $X^1\Sigma_\mathrm{g}^+$ for short C-C bond length then switches to $B^1\Delta_\mathrm{g}$ as the bond stretched, the wavefunctions of ground-state $X^1\Sigma_\mathrm{g}^+$ and $B^1\Delta_\mathrm{g}$ are used as initial guesses to obtain the whole curves for both states), (c) N-N triple-bond dissociation in N$_2$, and (d) P-P triple-bond dissociation in P$_2$. The total energies of two triplet C atoms, two quartet N atoms, and two quartet P atoms are set to zero for C$_2$, N$_2$, and P$_2$ respectively. The reference energies are: CEEIS results from ref. (38) for C$_2$, and MRCI+Q results from ref. (39) for both N$_2$ and P$_2$. All energies are in a.u.

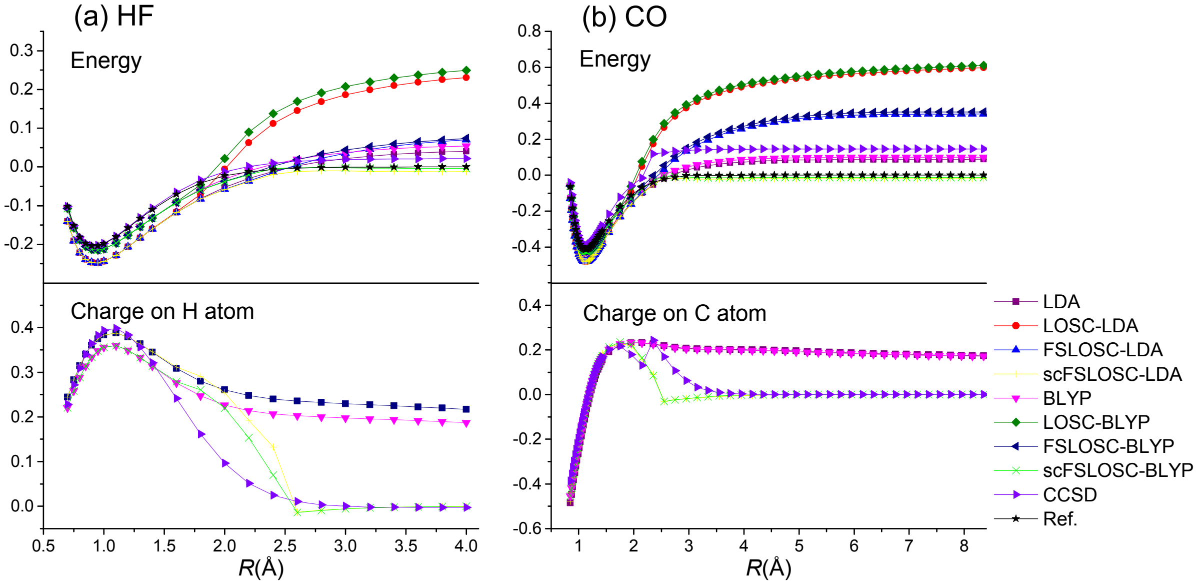

Fig. S7. (a) Potential energy curve and charge on H atom along H-F single-bond dissociation in HF; (b) Potential energy curve and charge on C atom along C-O multiple-bond dissociation in CO. The total energies of a doublet H atom and a doublet F atom, and a triplet C atom and a triplet O atom are set to zero for HF and CO respectively. Full CI results from ref. (40) and MRCI+Q results from ref. (41) are used as reference for HF and CO respectively. Both energies and charges are in a.u.

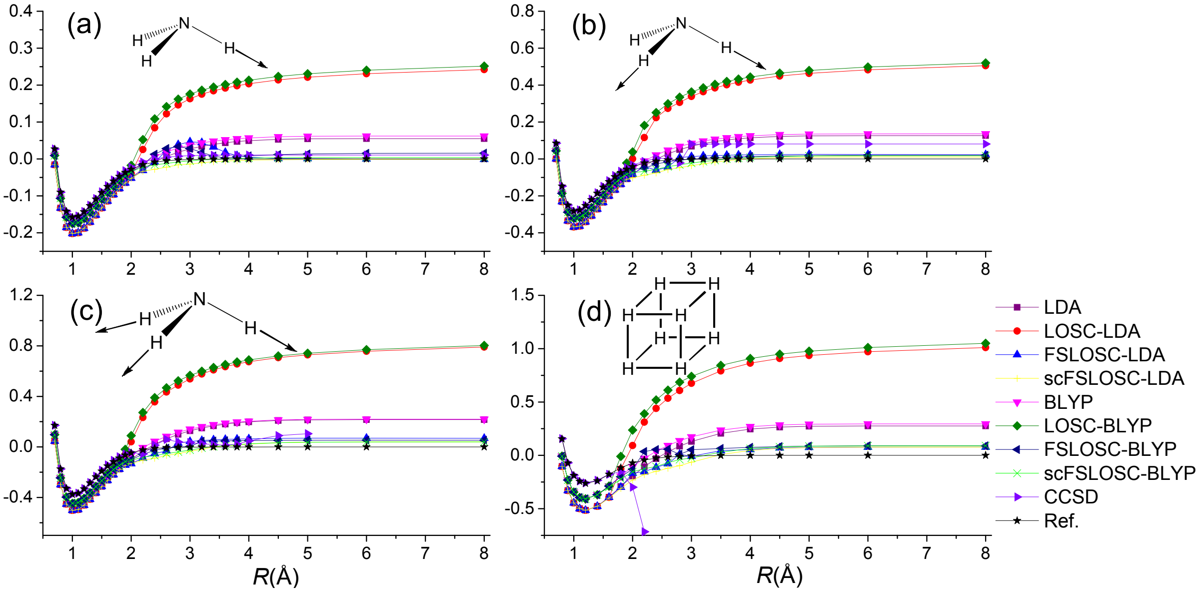

Fig. S8. Potential energy curves for (a) one N-H bond dissociation, (b) two N-H bonds dissociation at the same time, (c) all three N-H bonds dissociation at the same time in NH_3, and (d) outstretching all the eight H atoms in cubic hydrogens H_8. The total energies of a doublet H atom and a doublet NH_2 fragment, two doublet H atoms and a triplet NH fragment, three doublet H atoms and a quartet N atom, and eight doublet H atoms are set to zero for (a), (b), (c) and (d) respectively. The calculated Full CI results are used as reference. All energies are in a.u.

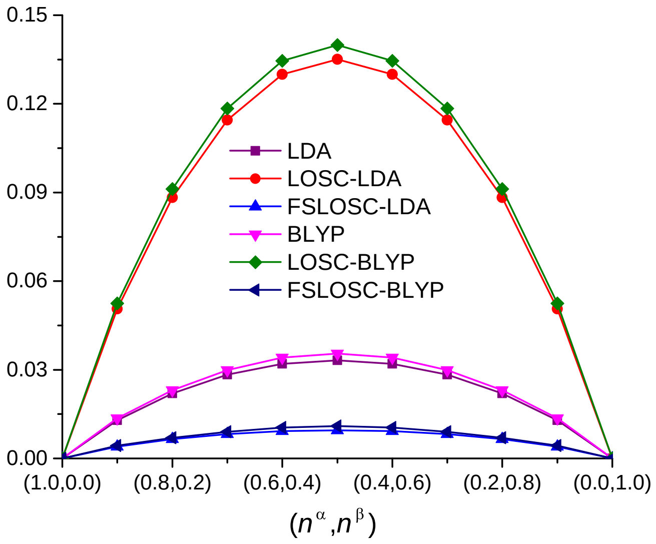

Fig. S9. Energies for H atom with fractional spins. The energy of integer-spin state, H(1,0), is set to zero. All energies are in a.u.

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