

Self-Consistent Calculation of Localized Orbital Scaling Correction for Correct Electron Densities and Energy Level Alignment in Density Functional Theory

Yuncai Mei,[†] Zehua Chen,[†] and Weitao Yang^{*,†,‡,¶}

[†]*Department of Chemistry, Duke University, Durham, North Carolina 27708, USA*

[‡]*Department of Physics, Duke University, Durham, North Carolina 27708, USA*

[¶]*Key Laboratory of Theoretical Chemistry of Environment, School of Chemistry and
Environment, South China Normal University, Guangzhou 510006, China*

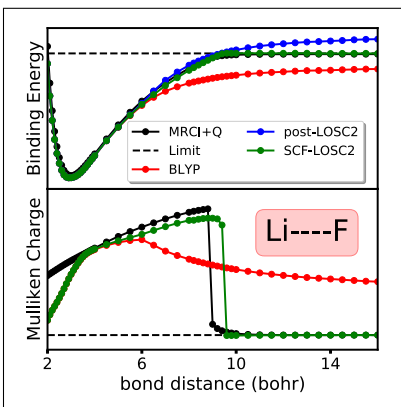
E-mail: weitao.yang@duke.edu

¹Y.M. and Z.C. contributed equally to this work and share the first authorship.

Abstract

The recently developed localized orbital scaling correction (LOSC) method shows the ability to systematically and size-consistently reduce the delocalization error existing in conventional density functional approximations (DFAs). However, the application of LOSC to DFAs was mainly through a post self-consistent field (SCF) manner, and few results from applying LOSC to DFAs with a SCF manner have been reported. The reason is that the originally proposed SCF approach for SCF-LOSC calculation uses an approximate Hamiltonian and encounters convergence problems easily in practice. In this work, we develop a new SCF approach with a correct Hamiltonian and achieve reliable SCF-LOSC calculations. We demonstrate the capability of the new SCF approach for SCF-LOSC to correctly describe the electron densities, total energies and energy level alignment for the molecular dissociation process, while conventional DFAs or LOSC-DFAs with post-SCF calculations show large errors. This work demonstrates that the new SCF approach for SCF-LOSC would be a promising method to study problems for correct electron densities and energy level alignment in large systems.

Graphical TOC Entry



Density functional theory (DFT)¹⁻³ has been widely used to calculate and predict the electronic structure of molecular systems in practice. The performance of DFT depends on the quality of applied density functional approximation (DFA) to the exchange-correlation energy E_{xc} . Although the conventional DFAs, such as local density approximation (LDA),^{4,5} general gradient approximations (GGAs)⁶⁻⁸ and hybrid GGAs,⁹⁻¹¹ are commonly used in practice, they all have the delocalization error¹²⁻¹⁵ and fail to describe some critical problems.

The delocalization error in conventional DFAs^{12,16} manifests a size-dependent manner as follows. (1) For systems with small numbers of atoms and a small physical extent, commonly used DFAs have good accuracy for describing the total energies of systems with integer number of electrons, but the delocalization error exhibits as the convex deviation from the Perdew-Parr-Levy-Baldur (PPLB) linearity condition for systems with fractional numbers of electrons.¹⁷⁻¹⁹ (2) For systems with large numbers of atoms, commonly used DFAs have small errors for systems with fractional numbers of electrons and obey the fractional charge linearity condition at the bulk limit, but the delocalization error manifests as the large errors in total energies for systems with integer number of electrons. (3) For systems with a finite number of atoms but with a large physical extent (as near a dissociation limit), the delocalization error leads to errors for total energies of systems with integer electron numbers and produces the convex deviation from the PPLB condition for systems with fractional numbers of electrons. The cases of ionization energies for noniterating Helium clusters clearly demonstrate these three scenarios.¹⁶ (For Weitao, we only discuss the impact of delocalization error to total energy in this paragraph.)

(For Weitao, starting from paragraph, we discuss about the outcomes from the error in total energies to connect with the previous paragraph.) Such delocalization error in conventional DFAs, showing as either the convex deviation to PPLB condition (aforementioned point 1 and 3) or large errors for total energies of systems with integer number of electrons (aforementioned point 2), leads to major error for the energy derivatives with respect to the electron number, i.e. the chemical potentials.^{13,20} Thus, this error leads the conventional

DFAs to underestimate of the exact ionization potentials (IPs) from the HOMO (highest occupied molecular orbital) energies and the overestimation of electron affinities (EAs) from the LUMO (lowest unoccupied molecule orbital) energies. In addition to the chemical potential, delocalization error would produce too delocalized electron density, as the error falsely lowers the total energy of the system.^{12,14,15} Examples reflecting this issue are the wrong dissociation limits of molecules^{21–25} and the underestimation of reaction barriers¹⁵ from conventional DFAs. For charge transfer complexes, delocalization error leads to overestimate of charge transfer and the binding energies.¹⁴ In material interfaces and defects, delocalization error can lead to incorrect charge transfer across the interfaces, and significant error in energy level alignment.^{26–29} Interfaces and energy level alignment play important roles in many technological applications: they strongly influence the charge extraction and transport in solar cell devices,³⁰ and catalysis in semiconductors.³¹ Thus it remains an important challenge to describe the correct energy level alignment for interfaces with DFAs.

To reduce the delocalization error, there has been much effort devoted to develop improved functional approximations. These include the development of long-range corrected functionals^{32–43} and double hybrid functionals.^{44–48} These methods have been shown to reduce delocalization error. But challenges still remain for a systematic correction across system types, sizes and scales.

Recently, our group developed the localized orbital scaling correction (LOSC) method, which imposes the PPLB condition by utilizing orbitalets (a set of molecular orbitals localized on both physical and energy space) to the associated parent DFAs to reduce the delocalization error.^{16,49} Benefiting from the novel features of orbitalets that dynamically switch between the canonical orbitals (COs) and localized orbitals (LOs), correction from LOSC can be flexibly and automatically applied on the global or local region of the system. Thus, LOSC shows the ability to reduce the delocalization error in a systematic and size-consistent way. LOSC has been shown to improve greatly the prediction of quasiparticle energies – ionization energies, electron affinities, and also ionized excited state energies for

atoms, small molecules and very large systems, all from the eigenvalues of the generalized Kohn-Sham Hamiltonian.^{16,49,50} The LOSC prediction accuracy is similar or better than the many-electron Green’s function method of GW.⁵⁰

In the original LOSC paper,¹⁶ two approaches for applying LOSC to the parent DFAs have been discussed. One way is in the post self-consistent field approach (post-LOSC), in which the converged electron density from the parent DFA (ρ_s^{DFA}) is directly used to evaluate the energy correction ΔE^{LOSC} from LOSC. The other way is the self-consistent field approach (SCF-LOSC), in which the LOSC effective Hamiltonian $\Delta h^{\text{LOSC}} = \frac{\delta \Delta E^{\text{LOSC}}}{\delta \rho_s}$ is introduced to the DFA Hamiltonian h_s^{DFA} . After solving the KS-equations with updated Hamiltonian $h_s = h_s^{\text{DFA}} + \Delta h^{\text{LOSC}}$ self-consistently, the converged electron density from LOSC-DFA ($\rho_s^{\text{LOSC-DFA}}$) is obtained and the correction ΔE^{LOSC} is therefore evaluated based on $\rho_s^{\text{LOSC-DFA}}$. In practice, the originally proposed SCF approach¹⁶ for the SCF-LOSC calculation tends to encounter convergence problems easily, especially for the calculations of large molecules, because only an approximate form of the LOSC effective Hamiltonian has been developed and used. Therefore, only the performance of post-LOSC has been well investigated. Although the post-LOSC has been demonstrated to show much improvement in the description of band gaps, total energies and photoemission spectra,^{16,49,50} the development of reliable SCF-LOSC approach is still necessary because of the following. First, in addition to energetic properties (total energies and orbital energies), the electron density of a molecular system is also an important property, since it closely relates to the molecule’s geometry, chemical bonding and reaction reactivities. The conventional DFAs, suffering from the delocalization error, produce much delocalized electron density and underestimate total energy in many cases.^{21–25,51} Applying post-LOSC in these cases is not sufficient because it only improves the energies for the parent DFA but leaves the significant error in electron density unchanged. Second, post-LOSC, being an reasonable approximation to the SCF-LOSC, is only valid at the condition that ρ_s^{DFA} is close to $\rho_s^{\text{LOSC-DFA}}$. When ρ_s^{DFA} differs much from $\rho_s^{\text{LOSC-DFA}}$ as the delocalization error from the parent DFA becomes significant, the

post-LOSC may not provide reliable results due to the lack of self-consistency, and applying SCF-LOSC calculation becomes necessary.

In this work, we present a new and robust SCF approach to achieve reliable SCF-LOSC calculations. We start with reviewing the methodology of LOSC. LOSC is designed to impose the PPLB linearity condition locally to conventional DFAs by using orbitalets (LOs, $\{\phi_i\}$). The orbitalets are molecular orbitals localized in both the physical and energy space and can be obtained through the LOSC localization procedure. Taking the localization in the developed version of LOSC (LOSC2)⁴⁹ as an example, the LOSC localization cost functional F takes the following form,

$$F(\rho_s, \{\psi_i\}, \mathbf{U}) = (1 - \gamma) \sum_p \left(\langle \mathbf{r}^2 \rangle_p - \langle \mathbf{r} \rangle_p^2 \right) + \gamma C \sum_p \left(\langle h[\rho_s]^2 \rangle_p - \langle h[\rho_s] \rangle_p^2 \right), \quad (1)$$

where

$$\langle X \rangle_p = \langle \phi_p | X | \phi_p \rangle, \quad X = \mathbf{r}, \mathbf{r}^2, h, h^2, \quad (2)$$

$$\text{and } \phi_p = \sum_i U_{pi} \psi_i, \quad (3)$$

$\mathbf{U}$ is the unitary transformation matrix, h is the one-electron Hamiltonian of the associated DFA evaluated at the electron density ρ_s at each SCF cycle, and $\{\psi_i\}$ are the corresponding COs. Through the LOSC localization, the obtained LOs are unitarily transformed from both occupied and virtual COs. Based on these LOs, the energy correction from LOSC (ΔE^{LOSC}) is constructed to restore the linearity condition. ΔE^{LOSC} is expressed as

$$\Delta E^{\text{LOSC}} = \sum_{ij} \frac{1}{2} \kappa_{ij} \lambda_{ij} (\delta_{ij} - \lambda_{ij}), \quad (4)$$

in which κ is the LOSC curvature matrix and λ is the local occupation matrix. The LOSC curvature and local occupation matrices are directly generalized from the global scaling correction (GSC) method.⁵² In contrast to GSC that constructs the curvature from COs

and uses canonical occupation numbers to provide corrections globally, LOSC evaluates the curvature based on LOs and uses local occupation numbers $\{\lambda_{ij}\}$ to impose the PPLB linearity condition locally. The LOSC curvature matrix has different expressions in different versions of LOSC. We call the original version of LOSC as LOSC1¹⁶ and the later version as LOSC2⁴⁹ in the following text. No matter in which version of LOSC, the LOSC curvature matrix is completely and explicitly determined by LOs. For example, the curvature matrix from LOSC1 is defined as

$$\kappa_{ij} = \int \frac{\rho_i(\mathbf{r})\rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' - \frac{2\tau C_x}{3} \int [\rho_i(\mathbf{r})]^{\frac{2}{3}} [\rho_j(\mathbf{r})]^{\frac{2}{3}} d\mathbf{r}, \quad (5)$$

in which $\rho_i(\mathbf{r})$ is the local orbital's density and defined as $\rho_i(\mathbf{r}) = |\phi_i(\mathbf{r})|^2$. The local occupation matrix λ is determined by LOs and the KS density operator ρ_s , and it is expressed as

$$\lambda_{ij} = \langle \phi_i | \rho_s | \phi_j \rangle. \quad (6)$$

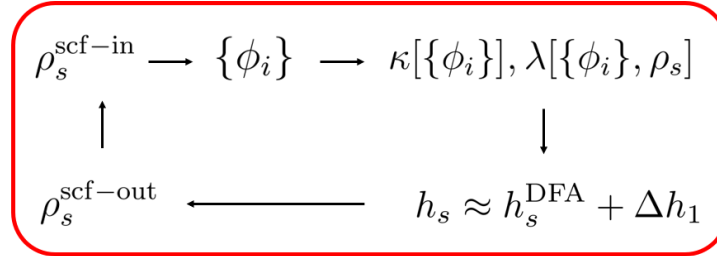


Figure 1: The original SCF procedure with the approximate LOSC effective Hamiltonian.

With the defined LOs, LOSC curvatures and local occupation numbers, the original SCF procedure for SCF-LOSC¹⁶ was proposed and the working flow is shown in Figure 1. As shown in Figure 1, one should notice that both LOs and electron density are updated in every SCF cycle. The dependence of LOs on the electron density (as defined in Eq. 1) in each SCF cycle introduces complexities for deriving the exact LOSC effective Hamiltonian. Specifically, according to the original SCF procedure and Eqs. 4 - 6, the exact LOSC effective

Hamiltonian Δh^{LOSC} for the original SCF approach is given by

$$\Delta h^{\text{LOSC}} = \frac{\delta \Delta E[\{\phi_i\}, \rho_s]}{\delta \rho_s} = \frac{\delta \Delta E}{\delta \rho_s} \Big|_{\{\phi_i\}} + \sum_i \frac{\delta \Delta E}{\delta \phi_i} \Big|_{\rho_s} \frac{\delta \phi_i}{\delta \rho_s} + \sum_i \frac{\delta \Delta E}{\delta \phi_i^*} \Big|_{\rho_s} \frac{\delta \phi_i^*}{\delta \rho_s}. \quad (7)$$

The first term (denoted as Δh_1) on the r.h.s. of Eq. 7 is the explicit contribution with the LOs fixed, and the last two terms (denoted as Δh_2) are the implicit contribution from the relaxation of LOs because of the dependence on electron density. Due to the difficulty of evaluating Δh_2 , the Δh_2 term was ignored in practical calculations. As shown in Figure 1, the LOSC effective Hamiltonian is approximated with only the Δh_1 term,

$$\Delta h^{\text{LOSC}} \approx \Delta h_1 = \sum_i \kappa_{ii} \left(\frac{1}{2} - \lambda_{ii} \right) |\phi_i\rangle \langle \phi_i| - \sum_{i \neq j} \kappa_{ij} \lambda_{ij} |\phi_i\rangle \langle \phi_j|. \quad (8)$$

However, such approximate LOSC effective Hamiltonian is not robust in practice, because we find it easily leads to SCF convergence difficulty. To solve the convergence problem, one straightforward solution is to derive the Δh_2 term to use the exact LOSC effective Hamiltonian. However, this would be complicated and difficult to achieve.

In this paper, we develop an alternative solution to the problem. The idea is to define a new SCF procedure with the removal of LOs' dependence on the electron density in each SCF cycle. The key step is to redefine the LOSC localization procedure, in another word, the localization cost functional. Instead of defining the LOSC localization cost functional that is dependent on the electron density and COs in each SCF cycle as shown in Eqs. 1 - 3, we can just use the electron density ρ_s^{DFA} and the corresponding COs $\{\psi_i^{\text{DFA}}\}$ from a converged DFA calculation in the cost functional. Therefore, we obtain a set of predetermined LOs $\{\phi_i^0\}$ in advance of the SCF-LOSC calculation and keep the same set of LOs $\{\phi_i^0\}$ during the SCF procedure. Applying this strategy to LOSC2 as an example, the modified localization

cost functional is expressed as

$$F(\rho_s^{\text{DFA}}, \{\psi_i^{\text{DFA}}\}, \mathbf{U}) = (1 - \gamma) \sum_p \left(\langle \mathbf{r}^2 \rangle_p - \langle \mathbf{r} \rangle_p^2 \right) + \gamma C \sum_p \left(\langle h[\rho_s^{\text{DFA}}]^2 \rangle_p - \langle h[\rho_s^{\text{DFA}}] \rangle_p^2 \right), \quad (9)$$

where

$$\langle X \rangle_p = \langle \phi_p^0 | X | \phi_p^0 \rangle, \quad X = \mathbf{r}, \mathbf{r}^2, h, h^2, \quad (10)$$

$$\text{and } \phi_p^0 = \sum_i U_{pi} \psi_i^{\text{DFA}}, \quad (11)$$

h is now evaluated at the ρ_s^{DFA} and LOs are unitarily transformed from the converged $\{\psi_i^{\text{DFA}}\}$. Clearly, the LOs in this new SCF approach do not depend on the electron density of each SCF cycle. This treatment of LOs in the new approach makes the Δh_2 term in Eq. 7 vanish and gives the exact LOSC Hamiltonian only with the Δh_1 term immediately; that is,

$$\Delta h^{\text{LOSC}} = \frac{\delta \Delta E[\{\phi_i^0\}, \rho_s]}{\delta \rho_s} = \sum_i \kappa_{ii} \left(\frac{1}{2} - \lambda_{ii} \right) |\phi_i^0\rangle \langle \phi_i^0| - \sum_{i \neq j} \kappa_{ij} \lambda_{ij} |\phi_i^0\rangle \langle \phi_j^0|. \quad (12)$$

The LOSC curvature is determined by the set of $\{\phi_i^0\}$, and it only needs to be evaluated once. The local occupation matrix is evaluated based on $\{\phi_i^0\}$ and electron density during the SCF procedure; that is, $\lambda_{ij} = \langle \phi_i^0 | \rho_s | \phi_j^0 \rangle$.

The working flow of the new SCF procedure for SCF-LOSC calculation is demonstrated in Figure 2. It involves the following steps: (1) carry out the SCF convergence from the parent DFA to get the converged electron density ρ_s^{DFA} and COs $\{\psi_i^{\text{DFA}}\}$; (2) apply the LOSC localization procedure to generate $\{\phi_i^0\}$ based on ρ_s^{DFA} and $\{\psi_i^{\text{DFA}}\}$; (3) construct and store the curvature matrix evaluated from $\{\phi_i^0\}$; (4) use the ρ_s^{DFA} as the initial guess to start the SCF-LOSC calculation associated with parent DFA; (5) use the density ρ_s from current SCF cycle to construct the DFA Hamiltonian h_s^{DFA} ; (6) evaluate local occupation matrix based on ρ_s and $\{\phi_i^0\}$, and construct the exact LOSC effective Hamiltonian Δh^{LOSC} via Eq.

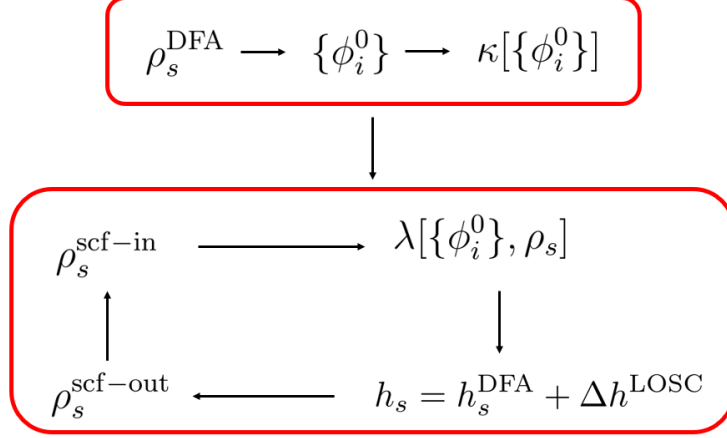


Figure 2: The new SCF procedure with the exact LOSC Hamiltonian.

12; (7) apply Δh^{LOSC} to h_s^{DFA} and update COs and ρ_s ; (8) check the convergence and go back to step (5) if it is not converged.

In the new SCF-LOSC approach, since the LOSC curvature matrix only needs to be evaluated once and updating the local occupation, $\lambda_{ij} = \langle \phi_i^0 | \rho_s | \phi_j^0 \rangle$, is simple, the computational cost for the new SCF-LOSC approach is only about two times that of the conventional DFA SCF calculation. Specifically, one is the generation of LOs from a one-time conventional DFA SCF calculation, and the other is the SCF-LOSC calculation with the corrected KS Hamiltonian, with fixed LOs and LOSC curvature matrix.

Comparing the new SCF approach with the original one, the solution from the new SCF approach may be different from the original SCF-LOSC solution. This is because, at the SCF solution point, the LOs used to evaluate the total energy in the new SCF-LOSC approach are always obtained from ρ_s^{DFA} , rather than $\rho_s^{\text{LOSC-DFA}}$. The significance of this difference needs to be verified with numerical results. If the relaxation of LOs, like in the original SCF-LOSC, turns to be necessary, we can apply an additional layer of SCF cycle on top of the new SCF-LOSC procedure in order to update the LOs. This two-layer SCF method is noted as macro-SCF-LOSC. Detailed procedure for the macro-SCF-LOSC is described in the supporting information. Ideally, because the macro-SCF-LOSC optimizes both electron density and LOs, the macro-SCF-LOSC should yield the same results as the original SCF-

LOSC approach. From the numerical results shown in the following main text, we find that the macro-SCF-LOSC is not necessary in practice, because the new SCF approach without the macro iteration is already able to provide reliable and excellent results.

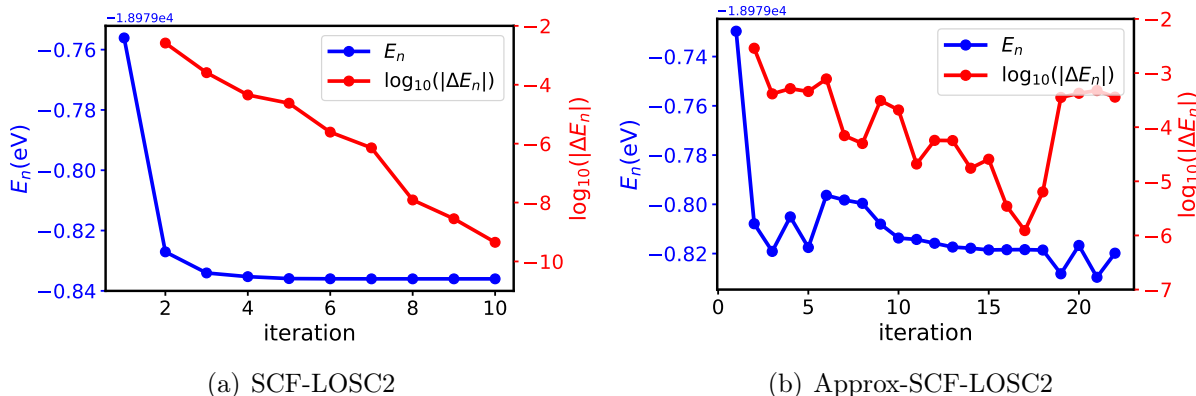


Figure 3: Comparison of SCF performance between (a) SCF-LOSC2 and (b) the original SCF-LOSC2 with approximate Hamiltonian (Approx-SCF-LOSC2) for polyacetylene ($n = 9$). E_n is the total energy at n -th iteration step and $\Delta E_n = E_n - E_{n-1}$. BLYP is used as the parent functional. 6-31g* is used as the basis set. aug-cc-pVTZ-RIFIT is used as the density fitting basis in LOSC2 curvature matrix construction.

Now, we check the performance of the new SCF approach for SCF-LOSC calculations. In the following text, the results from SCF-LOSC refer to the new SCF approach, if not specified otherwise. We first study the SCF convergence by testing a long organic molecule, the polyacetylene with 9 units of monomer ($[C_2H_2]_9$). As shown in Figure 3, the original SCF approach with the approximate LOSC effective Hamiltonian shows oscillation for total energy along the iterative steps, and it can not reach to the convergence after about 20 steps. The new SCF procedure with the exact LOSC effective Hamiltonian converges smoothly and quickly.

Next, we study the effect of initial guess in the new SCF approach. Note that in step (4) of the new SCF procedure, we use ρ_s^{DFA} as the SCF initial guess. This is necessary because the geometric orientation of LOs are fixed in the SCF process. Using ρ_s^{DFA} as the initial guess ensures the orientation of the LOs agree with the one of initial density and initial COs at the beginning. If the used initial electron density has a different orientation than that of

the LOs, it will artificially produce fractional local occupation numbers at the initial step, which may lead the SCF calculation converge to unphysical states with wrong energies. To support the discussion, Table 1 shows results for the test on F atom, with a partially filled p shell. For such small system, the LOs from LOSC localization are just the converged COs from the parent DFA. In other words, the localization is not operative and orbitals are just the COs for small systems. As shown in Table 1, if we use the non-rotated ρ_s^{DFA} as the initial guess, the local occupation numbers will be exact integer (either 1 or 0), and LOSC (both LOSC1 and LOSC2) gives zero correction to the total energy of the parent DFA. However, if we use the rotated ρ_s^{DFA} as the initial guess, which has a set of rotated p orbitals, the fractional local occupation numbers will be generated artificially and LOSC gives non-zero correction to the total energy of the parent DFA. In the case of LOSC1, we can see such artificial correction is even negative and leads to a unphysical state with energy even lower than DFA. In the case of LOSC2, the artificial energy correction is much smaller. This is because LOSC2 preserves the symmetry better than LOSC1,⁴⁹ making these artificial energy corrections from each fractional local occupation number almost canceled with each other. As a whole, to avoid issues introduced by the orientation of the initial guess, we use the ρ_s^{DFA} as the initial guess for the new SCF approach. Note, the choices of LO orientation will not be an issue at all, if the macro-SCF-LOSC is used, because the LO will be generated from $\rho_s^{\text{LOSC-DFA}}$ in the macro iterations.⁵³

With the smooth convergence from the new SCF procedure, we investigate the new SCF-LOSC with the same test sets used in the development of LOSC to test the performance for the atomization energies, reaction barriers, first ionization potentials (IPs) and electron affinities (EAs). Detailed results are documented in the supporting information. In general, the new SCF-LOSC can be conducted easily in these test sets. For the test sets related to atomization energies and reaction barriers, both SCF-LOSC and post-LOSC currently preserve the performance as DFAs. For example, the mean absolute error (MAE) of G2-1 test set for atomization energies is 4.94 kcal/mol for BLYP, and 4.93 kcal/mol for both

Table 1: Testing on F atom for the effect of the orientation of initial guess to the new SCF-LOSC approach. BLYP is used as the parent functional. The converged densities from BLYP (rotated/non-rotated) are used as the initial guess. cc-pVTZ is used the basis set. aug-cc-pVTZ-RIFIT is used as the density fitting basis set in LOSC curvature matrix construction. Grid type is (99, 590).

Method	E^3	ΔE^4	$E_{\text{corr}}(\text{initial})^5$	$E_{\text{corr}}(\text{SCF})^6$
BLYP	-99.7522856431			
SCF-LOSC1: non-rotated ¹	-99.7522856430	6.31E-11	1.10E-14	1.30E-14
SCF-LOSC1: rotated ²	-99.7794002845	-2.71E-02	-2.68E-02	-2.71E-02
SCF-LOSC2: non-rotated ¹	-99.7522856430	6.31E-11	1.00E-14	8.00E-15
SCF-LOSC2: rotated ²	-99.7522340746	5.16E-05	5.27E-05	5.05E-05

¹The orientation of initial electron density matches the one of LOs. ²The orientation of initial electron density does not match the one of LOs. ³Total energy. ⁴Total energy difference between the SCF-LOSC and BLYP. ⁵LOSC energy correction at the first SCF cycle. ⁶LOSC energy correction at the last SCF cycle.

post-LOSC2-BLYP and SCF-LOSC2-BLYP. The MAE of HTBH38 test case for the reaction barriers is 7.67 kcal/mol for BLYP, 7.49 kcal/mol for post-LOSC2-BLYP, and 7.54 kcal/mol for SCF-LOSC2-BLYP. Such performance is expected because most of cases in these tests are with small molecular sizes and large orbital energy gaps between HOMO and LUMO, which makes orbitalets equal to the COs of the parent DFA and the local occupation matrix being diagonal with integer numbers (1 for occupied space and 0 for virtual space). According to energy correction from LOSC shown in Eq. 4, these integer local occupation numbers give zero correction to the total energies. Re-tuning the parameters in the LOSC localization cost function to obtain more balanced localization between the physical space and energy space should provide better performance.⁴⁹ However, this task is beyond the scope of current work and will be studied in the future. For the test sets related to IPs and EAs, new SCF-LOSC produces much improvement compared to the parent DFA, and its performance is very similar to the one from post-LOSC for the tested cases. For example, the MAE of IP test set shown in the supporting information is 4.50 eV for BLYP, and 0.62 eV for both post-LOSC2-BLYP and SCF-LOSC2-BLYP.

In the following, we mainly focus on presenting the results that can be significantly

different, all related to electron density and energy levels (quasiparticle energies) associated with the molecular binding/dissociation processes. We first investigate the dissociation of three diatomic molecules (LiF, LiH and HF). B3LYP^{6,7,54} is applied as the parent functional, because the SCF convergence from B3LYP can be easily reached at long bond distance for these molecules. Similar GGA calculations would show even larger delocalization error with charge density, but was not obtained because of the SCF failure for large bond lengths. Results from multireference configuration interaction method with the Davidson correction (MRCI+Q)⁵⁵⁻⁵⁷ are used as the reference and compared to the results from B3LYP, post-LOSC-B3LYP and SCF-LOSC-B3LYP. To study the description of electron density, we look at the Mulliken charges from Mulliken population analysis⁵⁸ and the relative total energy of the molecule to its dissociation limit along the dissociation process.

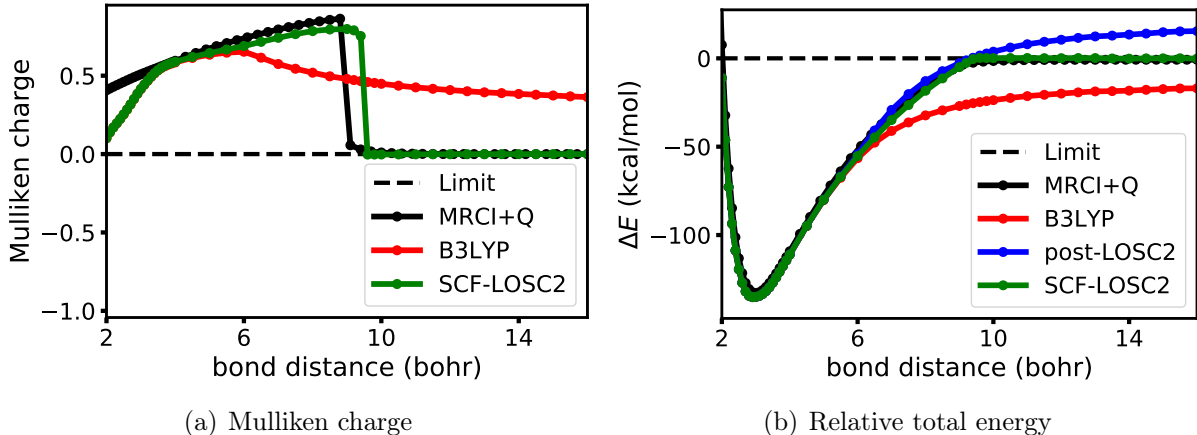


Figure 4: Dissociation of LiF molecule: (a) the Mulliken charge of Li atom; (b) the relative total energy of LiF with respect to Li and F atoms, $\Delta E = E_{\text{LiF}} - (E_{\text{Li}} + E_{\text{F}})$. LOSC2 calculations are associated with B3LYP.

Among the three diatomic molecules, B3LYP shows obvious delocalization error for LiF and LiH molecules, making them good cases to test the performance of the new SCF-LOSC approach. Thus, we highlight the results for LiF and LiH molecules in the main text. Results for HF molecule are documented in the supporting information. The results for LiF are shown in Figure 4. Because $\text{IP}_{\text{Li}} > \text{EA}_{\text{F}}$, the LiF molecule must dissociate into neutral Li and F atom (as with all neutral diatomic molecules). Clearly, according to Figure 4, we see B3LYP

shows significant delocalization error in electron density, which is reflected by the positive Mulliken charge of Li atom and underestimated dissociation energy at the dissociation limit. Based on the delocalized electron density from B3LYP, post-LOSC-B3LYP corrects the total energy too much and yields higher dissociation limit. In contrast to the post-LOSC-B3LYP, the SCF-LOSC-B3LYP corrects the electron density. As shown in Figure 4, the Mulliken charges from SCF-LOSC-B3LYP match well with the MRCI+Q reference. In addition, the relative total energies from SCF-LOSC-B3LYP almost overlap with the reference and shows the correct dissociation limit.

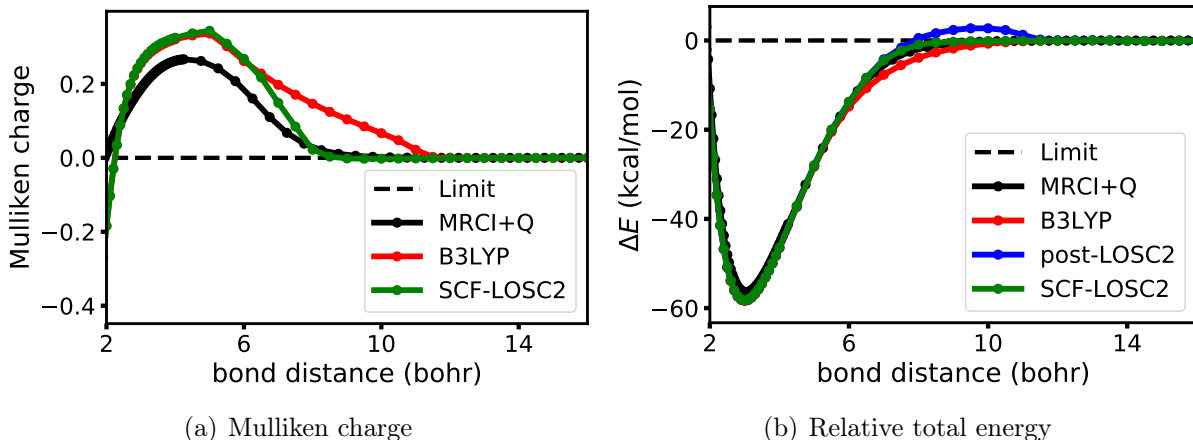


Figure 5: Dissociation of LiH molecule: (a) the Mulliken charge of Li atom; (b) the relative total energy of LiH with respect to Li and H atoms, $\Delta E = E_{\text{LiH}} - (E_{\text{Li}} + E_{\text{H}})$. LOSC2 calculations are associated with B3LYP.

Next, we look at the LiH molecule as shown in Figure 5. Because $\text{IP}_{\text{Li}} > \text{EA}_{\text{H}}$, the LiH molecule must dissociate into neutral Li and H atom. According to Figure 5, we notice that although B3LYP gives correct Mulliken charge (zero charge) of Li atom at the dissociation limit, it shows delocalization error at the bond length around 8-10 bohr, in which the MRCI+Q gives almost zero Mulliken charge while B3LYP gives positive charge. Such delocalized electron density (around 8-10 bohr) leads the relative total energy from B3LYP lower than the MRCI+Q reference. In addition, the error in electron density from B3LYP in the range of 8-10 bohr leads the post-LOSC-B3LYP to yield too high relative total energy, showing as the small bump in the dissociation energy curve in Figure 5. From the results of

SCF-LOSC-B3LYP, we observe that the electron density is corrected, showing as the Mulliken charge of Li in the range of 8-10 bohr is corrected down to zero. With the corrected electron density from SCF-LOSC-B3LYP, the relative total energy from SCF-LOSC-B3LYP matches much better with the MRCI+Q reference than B3LYP and post-LOSC-B3LYP.

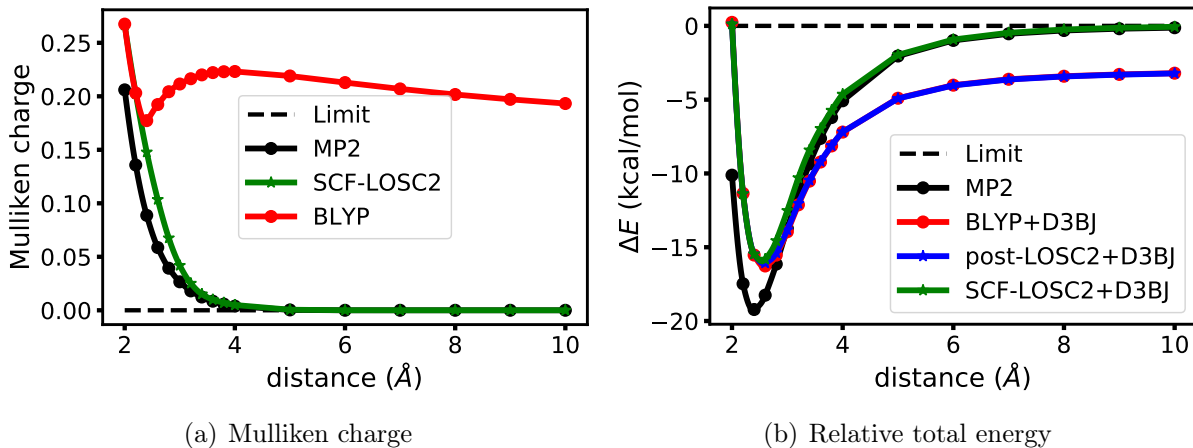


Figure 6: Dissociation of donor-acceptor (D-A) complex (donor: 1,4-benzenediamine, acceptor: tetracyanoethylene (TCNE)) from different methods: (a) the Mulliken charge of the donor molecule; (b) the relative total energy of D-A complex with respect to neutral donor and acceptor molecules, $\Delta E = E_{DA} - (E_D + E_A)$. LOSC2 calculations are associated with BLYP. The D3 version of Grimme’s dispersion with Becke-Johnson damping (D3BJ)⁵⁹ from BLYP functional is added to all the DFT energy results.

We also study a donor-acceptor (D-A) organic complex system to demonstrate the performance of new SCF-LOSC for more complicated and larger systems. The donor molecule is 1,4-benzenediamine and the acceptor molecule is tetracyanoethylene (TCNE). Because $IP_D > EA_A$, the D-A complex will dissociate into two neutral subsystems. Figure 6 shows the Mulliken charge results and the dissociation energy from DFT and MP2⁶⁰ calculations. BLYP is used as the parent function for DFT. Clearly, we see that the parent functional BLYP shows delocalization error at the dissociation limit. The donor molecule has spuriously positive charge, which means there is partial charge transferring from the donor to the acceptor molecule and the electron density is delocalized incorrectly. Due to the delocalized electron density from BLYP, the dissociation energy from BLYP and post-LOSC-BLYP shows similar error. With the correction to the electron density, we see that applying the

new SCF-LOSC gives the right Mulliken charges and total energies along the dissociation coordinates and including dissociation limit.

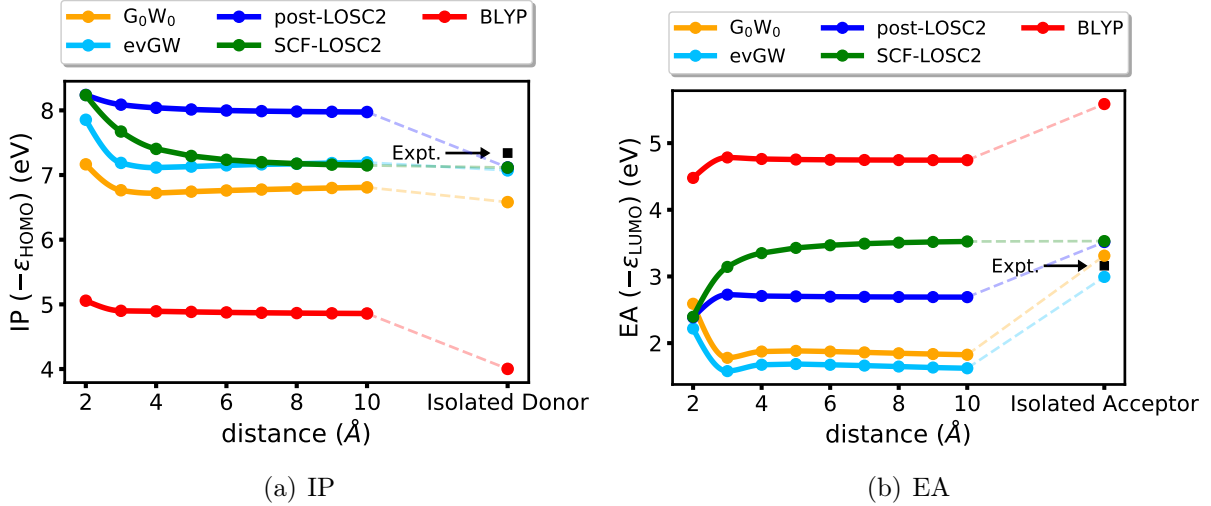


Figure 7: HOMO and LUMO energy level alignment of donor-acceptor (D-A) complex (donor: 1,4-benzenediamine, acceptor: tetracyanoethylene (TCNE)) from different methods: (a) the first IP ($-\epsilon_{\text{HOMO}}$) of D-A complex along the separation distance from 2 to 10 Å. At the right end of the figure, the first IP of the isolated donor molecule is plotted to be compared with the first IP from D-A complex calculations. The experimental IP of the isolated donor molecule is 7.34 eV⁶¹ and marked with an arrow. (b) the first EA ($-\epsilon_{\text{LUMO}}$) of D-A complex along the separation distance from 2 to 10 Å. At the right end of the figure, the first EA of the isolated acceptor molecule is plotted to be compared with the first EA from D-A complex calculations. The experimental EA of the isolated acceptor molecule is 3.16 eV⁶² and marked with an arrow. LOSC2 and GW calculations are based on BLYP.

In addition to the Mulliken charge analysis and dissociation energy of this D-A complex system, we examine its energy level alignment (the first IP and EA) along the binding distance. Figure 7 shows the trend of first IP and EA with respect to the change of separation distance. The experimental IP of the donor and EA of the acceptor molecule are plotted as the reference values for the dissociation limit. Along the binding distance, the D-A complex system is calculated with DFT and GW methods (G₀W₀ and eigenvalue self-consistent GW (evGW)). For the DFT calculations, the negative orbital energy of HOMO and the negative orbital energy of LUMO are used to evaluate the first IP and EA respectively.⁶³ For GW calculations, the obtained quasiparticle energies are used to evaluate the first IP and EA accordingly. According to Figure 7, we see BLYP shows significant underestimation of IP

and overestimation of EA because of the delocalization error. The results from GW method, which is based on BLYP functional, are also affected by the error in the electron density from BLYP. Especially in the case of EA, the results from GW shows obvious underestimation. At large distances, even at the level of evGW, the error in the EA energy level is underestimated by about 1.5 eV, which is significant. Since SCF-LOSC-BLYP corrects the electron density, the results from SCF-LOSC-BLYP are close to the reference value at the dissociation limit, especially for the first IP. The results from post-LOSC-BLYP, shows much improvement compared to the BLYP, however, they are not as good as SCF-LOSC-BLYP results.

The description of interface charge distribution and energy level alignment in this charge transfer system demonstrates the major improvement from the SCF-LOSC and clearly highlights the importance of getting correct density distributions through self consistent calculations, for the correct energy level alignment in DFT as well as in Green’s function calculations.

In summary, the new SCF-LOSC calculation overcomes the convergence issue and is very effective in practice. More importantly, we observe that the new SCF-LOSC approach is able to produce the correct electron densities, total energies and energy level alignment. The performance from SCF-LOSC is more reliable than the post-LOSC, especially for the cases in which the converged density from the parent DFA shows significant delocalization error. With the good performance and reliability, we believe the new SCF-LOSC method would be promising for studying problems related to electron densities, and quasiparticle energy level alignment in large molecules and interface systems.

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Supporting Information

Supporting Information Available: detailed results for the molecular dissociation, atomization energies, reaction barriers, IPs, EAs and detailed clarification of the macro-SCF-LOSC methodology.

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