

## Local Scaling Correction for Reducing Delocalization Error in Density Functional Approximations

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Delocalization error is one of the most fundamental and dominant errors that plagues presently used density functional approximations. It is responsible for a large class of problems in the density functional theory calculations. For an effective and universal alleviation of the delocalization error, we develop a local scaling correction scheme by imposing the Perdew-Parr-Levy-Baldurzi linearity condition to local regions of a system. Our novel scheme is applicable to various mainstream density functional approximations. It substantially reduces the delocalization error, as exemplified by the significantly improved description of dissociating molecules, transition-state species, and charge-transfer systems. The usefulness of our novel scheme affirms that the explicit treatment of fractional electron distributions is essentially important for reducing the intrinsic delocalization error associated with approximate density functionals.

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Despite the enormous success of density-functional theory (DFT), the mainstream density functional approximations (DFAs) often lead to various failures. Delocalization error [1–3] is one of the most fundamental and dominant errors that plagues the DFAs. Consequently, the local density approximation (LDA), the generalized gradient approximations (GGAs), and the hybrid functionals such as B3LYP [4,5] predict too high binding energies, too low reaction barriers, and too high electric polarizabilities for stretched molecules [2,3,6]. Other related problems include the underestimation of band gaps and the incorrect alignment of chemical potentials [7].

Delocalization error originates from the violation of the Perdew-Parr-Levy-Baldurzi (PPLB) condition [8–11], that the system energy as a function of electron number  $E(N)$  should be a straight line interpolating between integers. DFAs suffering from the delocalization error yield convex  $E(N)$  curves [1,7,10,12,13]. Inclusion of long-range Hartree-Fock (HF) exchange often makes  $E(N)$  curves straighter [14–19], and hence the range-separated DFAs have less severe delocalization error [17,18,20–26]. However, range separation schemes do not guarantee a complete cancellation of delocalization error. Delocalization error has also been related to electron self-interaction [6,12,15,27,28]. DFAs attempting to reduce the self-interaction error have been proposed [29–41], some of which, however, severely deteriorate the thermochemistry [3,34,40,41].

Universal alleviation of the delocalization error requires an explicit treatment of the fractional electron, which is missing in almost all the mainstream DFAs. Recently, several schemes have been proposed to deal with the fractional electron [42–44]. Zheng *et al.* have developed a nonempirical scaling correction (SC) scheme to retrieve the PPLB condition for systems with a fractional  $N$  [45]. For instance, the SC to the LDA energy functional is

$$\Delta E^{\text{SC-LDA}} = \frac{1}{2} \iint d\mathbf{r}d\mathbf{r}' \frac{[\rho(\mathbf{r}) - g(\mathbf{r})]|\phi_f(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} - \frac{1}{3} C_x \int d\mathbf{r} [\rho(\mathbf{r}) - g(\mathbf{r})] |\phi_f(\mathbf{r})|^2. \quad (1)$$

Here,  $C_x = \frac{3}{4}(6/\pi)^{1/3}$ ,  $g(\mathbf{r}) = \int d\mathbf{r}' \rho_s(\mathbf{r}, \mathbf{r}') \rho_s(\mathbf{r}', \mathbf{r})$ , with  $\rho_s(\mathbf{r}, \mathbf{r}')$  being the Kohn-Sham reduced density matrix, and  $\rho(\mathbf{r}) = \rho_s(\mathbf{r}, \mathbf{r})$  is the electron density. The key quantity is  $\rho(\mathbf{r}) - g(\mathbf{r}) = (n - n^2)|\phi_f(\mathbf{r})|^2$ , where  $n$  is the number of fractional electrons in the total system, and  $\phi_f(\mathbf{r})$  is the fractionally occupied orbital. The two terms on the right-hand side of Eq. (1) linearize the Hartree energy and the exchange energy at  $n \in [0, 1]$ , respectively. The inclusion of  $\Delta E^{\text{SC-LDA}}$  significantly improves the LDA predicted derivative band gaps for finite systems [45].

Despite the progress, the SC scheme has an obvious limitation—it fails to capture the fractional electron

distributions in integer- $N$  systems. Consequently, it gives zero correction to the electron density or the energy of any real physical system. For instance, It is well known that LDA and GGAs greatly underestimate the total energy of a dissociated  $\text{H}_2^+$  with half an electron on each proton, because of the severe delocalization error [2]. The SC of Eq. (1) gives  $\Delta E^{\text{SC-LDA}} = 0$ , since the whole  $\text{H}_2^+$  molecule has one integer electron.

To overcome such a limitation, in this Letter we propose a local scaling correction (LSC) scheme. The basic idea is to impose the PPLB condition to local pieces of a system. For a dissociated  $\text{H}_2^+$ , if we could impose the PPLB condition locally to the half electron on each proton and sum up the corrections, we would correct the total energy of the dissociated  $\text{H}_2^+$ .

One of the main challenges of LSC is how to extract the local distribution of the half electron from  $\rho_s(\mathbf{r}, \mathbf{r}')$  of a stretched  $\text{H}_2^+$ . In an atomic basis representation,  $\rho(\mathbf{r}) = \chi^T(\mathbf{r})\mathbf{P}\chi(\mathbf{r})$  and  $g(\mathbf{r}) = \chi^T(\mathbf{r})\mathbf{P}\mathbf{S}\mathbf{P}\chi(\mathbf{r})$ , where  $\chi(\mathbf{r})$  is the vector of basis functions  $\{\chi_i(\mathbf{r})\}$ , and  $\mathbf{P}$  is the Kohn-Sham reduced density matrix. Define  $\tilde{\mathbf{P}} = \mathbf{S}^{1/2}\mathbf{P}\mathbf{S}^{1/2}$ , where  $\mathbf{S} = \begin{bmatrix} S_A & \mathbf{0} \\ \mathbf{0} & S_B \end{bmatrix}$  is the basis overlap matrix, with  $A$  and  $B$  denoting the two protons (the off-diagonal matrix blocks are  $\mathbf{0}$  in the dissociation limit). For integer- $N$  systems, the eigenvalues of  $\tilde{\mathbf{P}}$  are either 1 or 0, and thus  $(\tilde{\mathbf{P}})^2 = \tilde{\mathbf{P}}$  and  $\rho(\mathbf{r}) - g(\mathbf{r}) = 0$ .

To capture the half electron, we replace  $\mathbf{S}$  by an  $\mathbf{r}$ -dependent screened overlap matrix  $S_v(\mathbf{r})$  with

$$S_{v,ij}(\mathbf{r}) = \int d\mathbf{r}' \chi_i(\mathbf{r}') v(|\mathbf{r} - \mathbf{r}'|) \chi_j(\mathbf{r}'), \quad (2)$$

and  $\tilde{\mathbf{P}}$  by  $\tilde{\mathbf{P}}_v(\mathbf{r}) = S_v^{1/2}(\mathbf{r})\mathbf{P}\mathbf{S}_v^{1/2}(\mathbf{r})$ . In Eq. (2),  $v(r) = 1$  at  $r < R_0$  ( $R_0$  is a certain length), while it decays quickly to 0 at  $r > R_0$ . At the position of proton A ( $\mathbf{r}_A$ ) or B ( $\mathbf{r}_B$ ), we have  $S_v(\mathbf{r}_A) = \begin{bmatrix} S_A & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{bmatrix}$  or  $S_v(\mathbf{r}_B) = \begin{bmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & S_B \end{bmatrix}$ . The eigenvalues of  $\tilde{\mathbf{P}}_v(\mathbf{r}_A)$  and  $\tilde{\mathbf{P}}_v(\mathbf{r}_B)$  are  $\{\frac{1}{2}, 0, \dots, 0\}$ . Here, the fractional eigenvalue  $\frac{1}{2}$  conveys the key information that each proton carries half an electron.

For general many-electron systems, the same  $S_v(\mathbf{r})$  and  $\tilde{\mathbf{P}}_v(\mathbf{r})$  can be defined. The eigenvalues of  $\tilde{\mathbf{P}}_v(\mathbf{r})$  are 1, 0, or a fractional number  $n_f(\mathbf{r})$ . We can thus extract  $n_f(\mathbf{r})$  by evaluating  $\tilde{\mathbf{P}}_v - (\tilde{\mathbf{P}}_v)^m$ . All the integer eigenvalues cancel exactly, while  $n_f(\mathbf{r}) - n_f(\mathbf{r})^m \approx n_f(\mathbf{r})$  provided that a large enough  $m$  is chosen [we take  $m = 10$  for  $n_f(\mathbf{r}) \sim 0.5$ ].

Besides the local fractional occupation number  $n_f(\mathbf{r})$ , its density distribution  $l(\mathbf{r})$  is also needed. Define

$$g_m^v(\mathbf{r}) = \int d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_m \rho_s(\mathbf{r}, \mathbf{r}_1) v(|\mathbf{r} - \mathbf{r}_1|) \rho_s(\mathbf{r}_1, \mathbf{r}_2) \times v(|\mathbf{r} - \mathbf{r}_2|) \cdots v(|\mathbf{r} - \mathbf{r}_m|) \rho_s(\mathbf{r}_m, \mathbf{r}). \quad (3)$$

$$l(\mathbf{r}) = \rho(\mathbf{r}) - \lim_{m \rightarrow \infty} g_{m-1}^v(\mathbf{r}) \\ = \lim_{m \rightarrow \infty} \chi^T(\mathbf{r}) S_v^{-1/2} [\tilde{\mathbf{P}}_v - (\tilde{\mathbf{P}}_v)^m] S_v^{-1/2} \chi(\mathbf{r}). \quad (4)$$

We may formally write  $l(\mathbf{r}) \equiv n_f(\mathbf{r})d(\mathbf{r})$ , with  $d(\mathbf{r})$  being the orbital density of the local fractional electron, as it plays an analogous role to  $|\phi_f(\mathbf{r})|^2$  in Eq. (1).

Consider also  $\tilde{\mathbf{Q}}_v(\mathbf{r}) = \mathbf{I} - \tilde{\mathbf{P}}_v(\mathbf{r})$  with  $\mathbf{I}$  being the identity matrix. The eigenvalues of  $\tilde{\mathbf{Q}}_v$  are complements to those of  $\tilde{\mathbf{P}}_v$ . Define similarly

$$\tilde{l}(\mathbf{r}) = \lim_{m \rightarrow \infty} \chi^T(\mathbf{r}) S_v^{-1/2} [\tilde{\mathbf{Q}}_v - (\tilde{\mathbf{Q}}_v)^m] S_v^{-1/2} \chi(\mathbf{r}). \quad (5)$$

The formal analogy between Eqs. (4) and (5) suggests that  $\tilde{l}(\mathbf{r}) = [1 - n_f(\mathbf{r})]d(\mathbf{r})$ , and hence  $d(\mathbf{r}) = l(\mathbf{r}) + \tilde{l}(\mathbf{r})$ .

Figure 1 depicts  $n_f(\mathbf{r})$  and  $d(\mathbf{r})$  versus the internuclear distance  $R$  of an  $\text{H}_2^+$  molecule. At a small  $R$  (say,  $R = 1 \text{ \AA}$ ),  $d(\mathbf{r})$  is rather small and  $n_f(\mathbf{r}) = l(\mathbf{r})/d(\mathbf{r}) \approx 0.9$  at  $\mathbf{r}$  near the nuclei. This indicates that there is a rather small amount of local fractional electron in a compact  $\text{H}_2^+$ , and hence the scaling correction to the total energy should be small. In contrast, at  $R \geq 5 \text{ \AA}$ ,  $d(\mathbf{r})$  exhibits two separated peaks with each at a proton site, and  $n_f(\mathbf{r}) \approx 0.5$  at the nuclear positions. The functions  $n_f(\mathbf{r})$  and  $d(\mathbf{r})$  thus reveal that each proton carries half an electron.

The remaining challenge is to construct a correction energy functional using  $l(\mathbf{r})$  and  $d(\mathbf{r})$  as basic variables. By making an analogy to Eq. (1), we design the following form of LSC (spin index is suppressed, and  $r = |\mathbf{r} - \mathbf{r}'|$ ):

$$\Delta E^{\text{LSC-LDA}} = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{l(\mathbf{r})u(\mu_0 r)[d(\mathbf{r}') - l(\mathbf{r}')] }{r} \\ - \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{l(\mathbf{r})[1 - u(\mu_0 r)]l(\mathbf{r}')}{r} \\ - C_x \int d\mathbf{r} \{l(\mathbf{r})[d(\mathbf{r})]^{1/3} - [l(\mathbf{r})]^{4/3}\}. \quad (6)$$

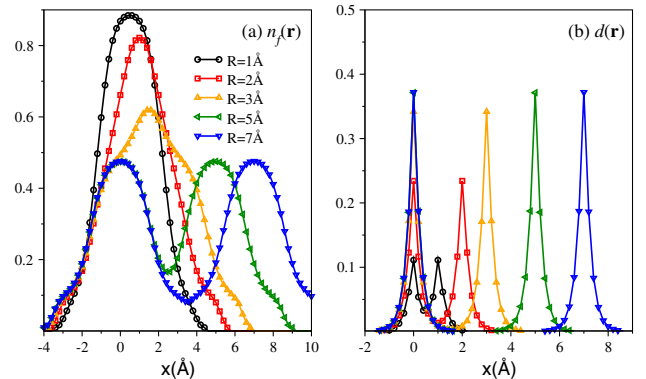


FIG. 1 (color online). (a) The local fractional occupation number  $n_f(\mathbf{r})$  and (b) the local fractional orbital density  $d(\mathbf{r})$  of a dissociating  $\text{H}_2^+$  along the bonding axis at various internuclear distances  $R$ . A proton locates at  $x = 0$ , while the other proton resides at  $x = R$ .

Here, the first and third terms on the right-hand side linearize the classical Coulomb and exchange energy densities at every  $\mathbf{r}$ , respectively. To achieve a truly local correction, a short-range kernel  $u(\mu_0 r)$  is introduced in the first term, with  $\mu_0$  being a range parameter. It limits the range of integration, so that only when  $\mathbf{r}$  and  $\mathbf{r}'$  are near the same nucleus, does the integrand contribute nontrivially to the energy. In practice, we adopt a Fermi-type form for  $u(\mu_0 r)$  [46], which gives a smooth spatial cutoff at a certain length. For simplicity, we set the cutoff length of  $u(\mu_0 r)$  to be the same as  $v(r)$ . The second term is to eliminate the unwanted long-range Coulomb repulsion between the two half-electrons at a large  $R$ , which is essential to attain the correct asymptotic behavior for the total energy as  $R \rightarrow \infty$ .

The LSC to DFAs other than LDA can be designed similarly. In this Letter we simply use  $\Delta E^{\text{LSC-GGA}} \approx \Delta E^{\text{LSC-LDA}}$  for GGAs, and  $\Delta E^{\text{LSC-B3LYP}} \approx (1-a_0)\Delta E^{\text{LSC-LDA}}$  for the hybrid functional B3LYP, with  $a_0 = 0.2$  being the weight of HF exchange.

Figure 2(a) depicts the energy of  $\text{H}_2^+$  versus  $R$  calculated by various DFAs. Compared with the exact HF curve, LDA, BLYP [5,47], and B3LYP drastically underestimate the energies at large  $R$ . DFAs containing long-range HF exchange such as LC-BLYP [17], LC- $\omega$ PBE [48],  $\omega$ B97 [26], and CAM-B3LYP [22] give improved energies, but the energies still deviate significantly from the exact curve at  $R > 3 \text{ \AA}$ . In contrast, LSC-DFAs yield energies very close to the exact curve at large  $R$ , which clearly affirms the validity of the LSC. Substantial improvement of energy by the LSC is also seen in Fig. 2(b), where the dissociation of  $\text{He}_2^+$  is examined.

The LSC gives almost no energy correction at small  $R$ , such as at the equilibrium bond length of  $\text{H}_2^+$  ( $R \approx 1 \text{ \AA}$ ). This is because  $n_f(\mathbf{r}) \approx 1$  (see Fig. 1) and  $l(\mathbf{r}) \approx d(\mathbf{r})$ . Note

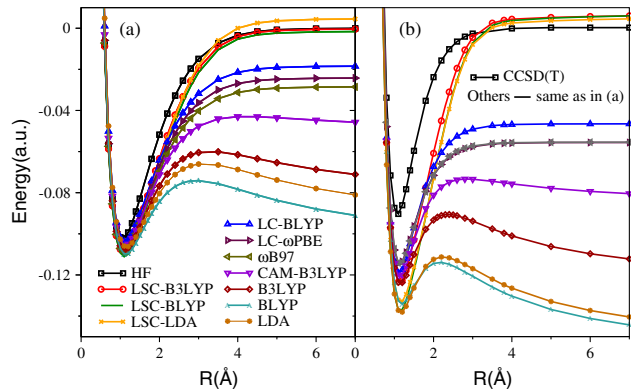


FIG. 2 (color online). Dissociation energy curves of (a)  $\text{H}_2^+$  and (b)  $\text{He}_2^+$ . The total energy of isolated H and  $\text{H}^+$  (He and  $\text{He}^+$ ) is set to zero energy.  $S_v(\mathbf{r})$  and  $\Delta E^{\text{LSC-LDA}}$  are calculated by Eqs. (2) and (6), respectively. For numerical convenience, both  $v(r)$  and  $u(\mu_0 r)$  are expanded by polynomial Gaussians [46], and their cutoff lengths are chosen to be around  $1 \text{ \AA}$ . For  $\text{He}_2^+$  the coupled-cluster method with single, double, and noniterative triple excitation [CCSD(T)] [49–51] is taken as reference.

that  $n_f(\mathbf{r})$  is slightly off the integer value 1 at  $\mathbf{r}$  near the nuclei. This is because  $S_v(\mathbf{r})$  differs slightly from  $S$  with a small cutoff length ( $R_0 = 1 \text{ \AA}$ ) chosen for  $v(r)$ .

We now consider general polyatomic systems. To have a universally applicable LSC, Eq. (6) needs to be modified. This is because (i) the long-range Coulomb term (the second term) will diverge in extensive systems such as in solids, (ii) the screening distance  $R_0$  for  $v(r)$  should be atom specific, and (iii) the computation of  $S_v(\mathbf{r})$  and  $\Delta E^{\text{LSC-DFA}}$  is rather expensive with Eqs. (2) and (6).

To resolve the above issues, we make the following change to Eq. (6). (i) We replace the long-range kernel  $1 - u(\mu_0 r)$  in the second term by a midrange kernel  $w(r) = u(\mu_1 r) - u(\mu_2 r)$ , to avoid possible divergence of energy. (ii) We adopt the approximation

$$S_v(\mathbf{r}) \approx \mathbf{S}^{1/2} \mathbf{V}(\mathbf{r}) \mathbf{S}^{1/2}, \quad (7)$$

with  $V_{ij}(\mathbf{r}) = \delta_{ij}(1 + e^{\beta[|\mathbf{r}-\mathbf{r}_i|-R_0(\mathbf{r})]})^{-1}$ . Here,  $\mathbf{r}_i$  is the center of  $i$ th atomic basis,  $\beta = 4.0 \text{ bohr}^{-1}$ , and  $R_0(\mathbf{r}) = R_{0i}$  at  $\mathbf{r}$  close to  $\mathbf{r}_i$ , with  $R_{0i}$  being an atom-specific radius [46]. (iii) We expand the kernels  $u(\mu_0 r)$  and  $w(r)$  by error functions and polynomial Gaussians, and use a resolution of the identity technique [52,53] to simplify the computation of the double integrals. All the parameters involved in the LSC, including the range parameters  $\{\mu_0, \mu_1, \mu_2\}$  and the atom-specific screening radii  $\{R_{0i}\}$ , are determined by minimizing the mean absolute error of the G2-1 set [54] of thermochemical data [46,55–57] non-self-consistently using orbitals of the parent DFAs. These parameters are then fixed for all other systems.

For a many-electron system with a compact geometry, the screening of core electrons by  $S_v(\mathbf{r})$  may lead to an artificial local fractional electron, making  $n_f(\mathbf{r}) < 1$  near the nuclei. This inevitably causes some minor overcorrection to the energy. As shown in Table I, compared with the parent DFAs, the LSC-DFAs largely preserve yet slightly compromise (due to the minor over-correction) the accuracy of thermochemical properties for molecules at equilibrium structures. In contrast, transition-state species involve partially formed or dissociated chemical bonds, and the existing local fractional electron distributions are

TABLE I. Performance of LSC-BLYP and LSC-B3LYP on thermochemical properties and reaction barriers. The HTBH38/08 and NHTBH38/08 test sets contain 38 hydrogen and non-hydrogen transfer reaction barrier heights [58,59], respectively. See the Supplemental Material [46] for more details.

Test set	Mean absolute error (kcal/mol)			
	BLYP	LSC-BLYP	B3LYP	LSC-B3LYP
HTBH38/08	7.83	4.85	4.43	2.71
NHTBH38/08	8.79	4.38	4.44	2.93
G2-97	7.28	7.41	3.40	4.51

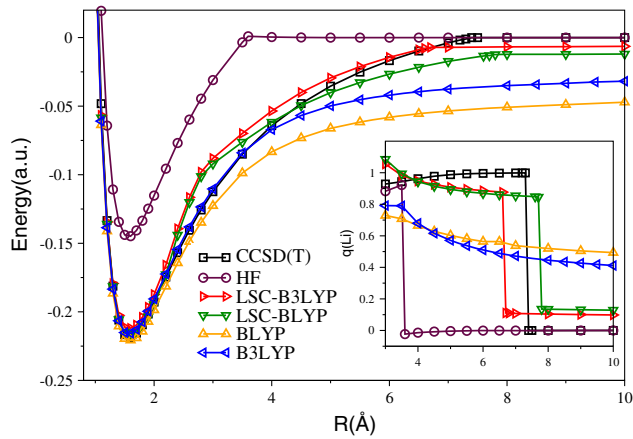


FIG. 3 (color online). Dissociation energy curves of a LiF molecule. The sum of energies of a neutral Li atom and a neutral F atom is set to zero energy. The inset shows the Mulliken charge on Li as a function of internuclear distance  $R$ .

well captured by the LSC. As seen from Table I, the LSC indeed significantly improves the prediction of hydrogen and nonhydrogen transfer reaction barrier heights.

The LSC is within the generalized Kohn-Sham scheme [60], since its form depends explicitly on  $\rho_s(\mathbf{r}, \mathbf{r}')$ . The corresponding correction to the Kohn-Sham Hamiltonian matrix  $\Delta H_{ij}^{\text{LSC}} = \partial \Delta E^{\text{LSC}} / \partial P_{ij}$  can be evaluated readily [46]. Therefore, all the LSC-DFA results reported below were obtained with self-consistent field calculations.

With the corrected Kohn-Sham Hamiltonian, the LSC is capable of correcting the wrong electron density resulting from the delocalization error. This is exemplified by the dissociation of a LiF molecule as shown in Fig. 3. The CCSD(T) method predicts that the Mulliken charge  $q$  on Li undergoes an abrupt jump from +1 to 0 at  $R = 7.4 \text{ \AA}$ , where the two energy surfaces corresponding to the ionic and neutral dissociation products intersect with each other. It is known that BLYP and B3LYP yield rather smooth  $q(\text{Li})$  versus  $R$  curve [41,61] because the delocalization error leads to the wrong electron density with fractional electron localized on each nucleus. With the LSC, the sharp transition in  $q(\text{Li})$  is recovered, and the energy at large  $R$  is also substantially corrected. This example clearly demonstrates the advantage of LSC in treating charge-transfer systems.

The validity of the LSC is independent of system size. This is because by construction the overall correction is the sum of all local contributions (integration over  $\mathbf{r}$ ). Therefore, LSC-DFAs are potentially useful for the studies of large complex systems. For instance, in a DFT-based molecular dynamics study of a water-solvated OH radical ( $\text{OH}\cdot$ ), the  $\text{OH}\cdot$  is predicted to carry a negative charge of  $-0.2$  by BLYP [62,63]. This is known to be an artifact caused by the delocalization error. We performed calculations on the clusters  $\text{OH}\cdot(\text{H}_2\text{O})_n$  ( $n = 1, \dots, 15$ ) with various DFAs. As shown in Fig. 4, while the BLYP predicts that  $q(\text{OH}\cdot)$  approaches to  $-0.2$

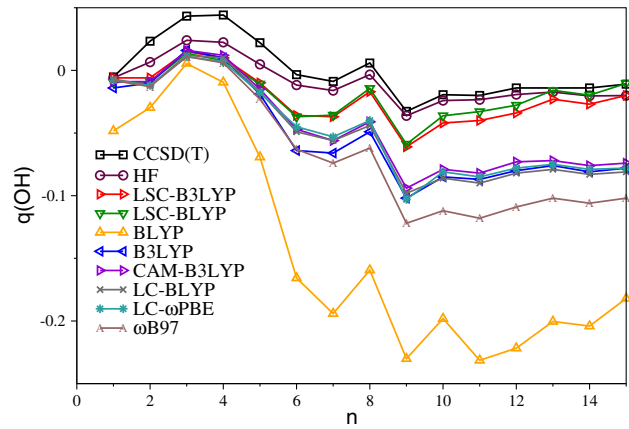


FIG. 4 (color online). Mulliken charge on  $\text{OH}\cdot$  (sum of atomic Mulliken charges on O and H) versus  $n$  for the clusters  $\text{OH}\cdot(\text{H}_2\text{O})_n$ .

as  $n$  increases, some hybrid or range-separated DFAs reduce  $q(\text{OH}\cdot)$  to about  $-0.1$ . In contrast, with the LSC-BLYP the unphysical negative charge on  $\text{OH}\cdot$  becomes negligibly small. Moreover, GGAs incorrectly predict a hemibonding geometry to be the energy minimum of  $\text{OH}\cdot\text{H}_2\text{O}$  [62,64], while LSC-GGAs correctly predict a hydrogen-bonding structure to be energetically more favorable [65].

To conclude, the proposed LSC scheme offers an effective and general approach for reducing the delocalization error of mainstream DFAs. It significantly improves the characterization of dissociating molecules, transition-state species, and charge-transfer systems within the framework of DFT. For systems with compact geometries, the present form of the LSC may lead to minor overcorrection.

It is known that range-separated DFAs yield accurate reaction barriers [3,22,26,48,66], and some long-range corrected DFAs such as LC-BLYP and  $\omega\text{B97}$  can properly dissociate a LiF molecule [46]. This is because the localization error associated with the long-range HF exchange cancels partly the delocalization error of the LDA or GGA exchange. However, a complete cancellation of errors is generally not guaranteed; see Figs. 2 and 4. Moreover, the optimal range-separation form can be rather system dependent [18,19,23,67]. In contrast, the LSC is based on a conceptually different strategy—it aims at a universal elimination of delocalization error by imposing the PPLB condition locally at every  $\mathbf{r}$ -point.

The LSC proposed in this Letter is much beyond the previously developed global SC scheme [45], as it is capable of correcting both the energy and the electron density of realistic physical systems. Therefore, it presents an important step forward along the direction of understanding and correcting the intrinsic errors of DFAs [2,3]. In addition, the present form of the LSC is expected to give nonzero corrections to periodic systems, and thus it would be interesting to study how the LSC affects the properties of solids and interfacial systems.



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