

Improving Band Gap Prediction in Density Functional Theory from Molecules to Solids

Xiao Zheng,¹ Aron J. Cohen,² Paula Mori-Sánchez,³ Xiangqian Hu,¹ and Weitao Yang¹

¹*Department of Chemistry, Duke University, Durham, North Carolina 27708, USA*

²*Department of Chemistry, Lensfield Road, University of Cambridge, Cambridge, CB2 1EW, United Kingdom*

³*Departamento de Química, Universidad Autónoma de Madrid, 28049 Madrid, Spain*

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A novel nonempirical scaling correction method is developed to tackle the challenge of band gap prediction in density functional theory. For finite systems the scaling correction largely restores the straight-line behavior of electronic energy at fractional electron numbers. The scaling correction can be generally applied to a variety of mainstream density functional approximations, leading to significant improvement in the band gap prediction. In particular, the scaled version of a modified local density approximation predicts band gaps with an accuracy consistent for systems of all sizes, ranging from atoms and molecules to solids. The scaled modified local density approximation thus provides a useful tool to quantitatively characterize the size-dependent effect on the energy gaps of nanostructures.

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Accurate prediction of band gaps is one of the critical challenges in density functional theory (DFT) with potential wide applications. The capability to predict gaps for systems of all sizes is critical for the study of material interfaces but currently remains out of reach within DFT.

For a system of N electrons (N is an integer) in an external potential $v(\mathbf{r})$, its fundamental (or integer) band gap is $E_{\text{gap}}^{\text{int}} = I - A$, where $I = E_v(N-1) - E_v(N)$ is the ionization potential and $A = E_v(N) - E_v(N+1)$ is the electron affinity. With n additional fractional electrons ($0 < n < 1$), the system energy as a function of n is given by the Perdew-Parr-Levy-Baldur condition [1]: It is a straight-line interpolation between energies at integer points, i.e., $E_v(N+n) = (1-n)E_v(N) + nE_v(N+1)$. Such a linear relation infers that, in principle, $E_{\text{gap}}^{\text{int}}$ should be exactly reproduced by the derivative gap, i.e., the difference between left and right energy derivatives at N : $E_{\text{gap}}^{\text{der}} \equiv \lim_{n \rightarrow 0} (\frac{\partial E_v}{\partial N}|_{N+n} - \frac{\partial E_v}{\partial N}|_{N-n}) = E_{\text{gap}}^{\text{int}}$. More specifically, the exact DFT should give $I = -\lim_{n \rightarrow 0} \frac{\partial E_v}{\partial N}|_{N-n}$ and $A = -\lim_{n \rightarrow 0} \frac{\partial E_v}{\partial N}|_{N+n}$ [1,2].

In the Kohn-Sham (KS) scheme [3] where the exchange-correlation (XC) energy is an explicit functional of electron density, i.e., $E_{\text{xc}} = E_{\text{xc}}[\rho(\mathbf{r})]$, it has been proved that $\frac{\partial E_v}{\partial N} = \epsilon_f$, with ϵ_f being the KS frontier orbital energy [2]. f is either the highest occupied molecular orbital (HOMO) if N is approached from $N-n$ or, otherwise, the lowest unoccupied molecular orbital (LUMO). Therefore, $E_{\text{gap}}^{\text{der}} = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$. The same situation applies to the generalized KS scheme, where $E_{\text{xc}} = E_{\text{xc}}[\rho_s(\mathbf{r}, \mathbf{r}')] / \rho_s(\mathbf{r}, \mathbf{r}')$ being the KS first-order reduced density matrix. Therefore, if the linearity condition could be satisfied, $I = -\epsilon_{\text{HOMO}}$, $A = -\epsilon_{\text{LUMO}}$, and thus $E_{\text{gap}}^{\text{der}} = E_{\text{gap}}^{\text{int}}$ should be realized in DFT [2].

The actual fractional charge behavior of $E_v(N+n)$ of standard density functional approximations (DFAs) is

summarized as follows. (i) The local density approximation (LDA) and the generalized gradient approximation (GGA) give reasonable I , A , and hence $E_{\text{gap}}^{\text{int}}$ for small systems. However, they predict much too high ϵ_{HOMO} and too low ϵ_{LUMO} and, thus, greatly underestimate $E_{\text{gap}}^{\text{der}}$. This is due to the delocalization error, which gives an overall convex energy curve [4]. (ii) The Hartree-Fock approximation gives less accurate energies at integers, due to the lack of electron correlation. Its significant localization error leads to a rather concave energy curve [5] and severe overestimation of $E_{\text{gap}}^{\text{der}}$. (iii) Hybrid and range-separated hybrid DFAs such as B3LYP [6], PBE0 [7], HSE [8], and HISS [9] have both convex and concave ingredients. The delocalization error is generally not compensated by the localization error, resulting in a convex energy curve and underestimation of $E_{\text{gap}}^{\text{der}}$ [10]. (iv) The self-interaction correction of Perdew and Zunger [11] straightens the LDA or GGA energy curve but significantly degrades the description of integers [12]. (v) Long-range corrected DFAs such as MCY3 [13] and rCAM—B3LYP [13] achieve the correct straight-line behavior [14]. They yield accurate $E_{\text{gap}}^{\text{int}}$ and $E_{\text{gap}}^{\text{der}}$ for atoms and small molecules, but the error increases significantly as the system size grows. Therefore, none of the existing DFAs is capable of predicting band gaps with consistent accuracy for systems of all sizes.

To fix this problem, we start with a DFA which gives reasonable band gaps for solids and then improve its prediction on atoms and molecules of all sizes. For bulk systems, the convexity of the LDA energy curve is suppressed by infinite system size [4]. However, the delocalization error remains at integers, resulting in significant underestimation of band gaps for nonmetallic solids by the LDA. Bylander and Kleinman [15] have combined screened Hartree-Fock exchange with the long-range LDA. The resulting DFA, the modified LDA (MLDA),

improves the band gap prediction for semiconductors. They used $\frac{\exp(-K_s r)}{r}$ as the screened Coulomb operator, with K_s being a function of $\rho(\mathbf{r})$ [15]. A different range-separation scheme, $\frac{1}{r} = \frac{\text{erf}(\mu r)}{r} + \frac{\text{erfc}(\mu r)}{r}$, has been popular in the DFT community [13,16,17]. Here, $\text{erf}(x)$ is the error function and $\text{erfc}(x) = 1 - \text{erf}(x)$. Employing the erf splitting and VWN5 [18] for correlation, we have

$$E_{\text{xc}}^{\text{MLDA}} = E_{\text{x}}^{\text{SR,HF}} + E_{\text{x}}^{\text{LR,LDA}} + E_{\text{c}}^{\text{LDA}}. \quad (1)$$

The form of $E_{\text{x}}^{\text{LR,LDA}}$ is given in Refs. [16,19]. We choose $\mu = 0.5 \text{ bohr}^{-1}$ as it is within the typical range for the splitting parameter [16]. Our calculations clearly indicate the MLDA systematically improves over the LDA; see Fig. 1. The MLDA gives a mean absolute error (MAE) of 0.22 eV for 13 covalent crystals with gaps below 7 eV. For large-gap ionic and noble gas crystals, the error increases with the gap, due to the weaker dielectric screening in these materials. Nevertheless, the MLDA still outperforms the LDA. For metals, the MLDA correctly predicts zero gaps [19]. We notice that other approaches have recently been proposed to improve solid band gaps [20,21].

Much like the LDA, the MLDA gives a convex energy curve for atoms and molecules. To achieve accurate $E_{\text{gap}}^{\text{der}}$ for finite systems, it is essential to reduce the delocalization error by restoring the linearity condition. The total electronic energy in DFT is $E_v = T_s + V_{\text{ext}} + J + E_{\text{xc}}$. With the KS orbitals fixed as the electron number is varied, the KS kinetic energy T_s and external potential energy V_{ext} are linear in $\rho(\mathbf{r})$, while the electron Coulomb energy $J[\rho]$ is quadratic, and $E_{\text{xc}}[\rho]$ is usually nonlinear in $\rho(\mathbf{r})$. Therefore, a linear $E_v(N+n)$ can be achieved by linearizing both $J[\rho]$ and $E_{\text{xc}}[\rho]$ with respect to n , the main goal of our scaling correction (SC) [19].

As the number of electrons increases from N to $N+n$, $\rho(\mathbf{r})$ varies as $\rho_{N+n}(\mathbf{r}) \approx \rho_N(\mathbf{r}) + n f(\mathbf{r})$, with

$f(\mathbf{r}) = \lim_{n \rightarrow 0} \frac{\partial \rho_{N+n}(\mathbf{r})}{\partial n} |_{v(\mathbf{r})}$ being the Fukui function [22]. Consider $g(\mathbf{r}) \equiv \int d\mathbf{r}' \rho_s(\mathbf{r}, \mathbf{r}') \rho_s(\mathbf{r}', \mathbf{r}) = \sum_{i \in \text{occ}} n_i^2 |\phi_i(\mathbf{r})|^2$, with $\phi_i(\mathbf{r})$ and n_i being the i th KS orbital and occupation number, respectively. At $0 < n < 1$, $\rho(\mathbf{r}) - g(\mathbf{r}) = (n - n^2) |\phi_f(\mathbf{r})|^2$, with $\phi_f(\mathbf{r})$ being the fractionally occupied KS orbital. The square of the spinless first-order reduced density matrix has been used for describing the distributions of odd electrons [23] and effectively unpaired electrons [24].

The SC to $J[\rho]$ is obtained as [19]

$$\Delta J(N+n) = \frac{n - n^2}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{f(\mathbf{r}) f(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \approx \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{[\rho(\mathbf{r}) - g(\mathbf{r})] |\phi_f(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}, \quad (2)$$

where $f(\mathbf{r}) \approx |\phi_f(\mathbf{r})|^2$ is used in the second step. At integer points, $\Delta J = 0$ due to $\rho(\mathbf{r}) = g(\mathbf{r})$. However, $\frac{\partial \Delta J}{\partial n}$ is non-zero at either $n = 0$ or 1 . This nonzero derivative gives a finite correction to ϵ_f and $E_{\text{gap}}^{\text{der}}$.

For the XC energy, only the exchange part is treated, since the SC to correlation energy is much smaller. The SC to exchange energy, $\Delta E_{\text{x}}^{\text{DFA}}$, can be obtained by exploring the scaling relation of exchange energy at fractional electron occupation. We derive the form of $\Delta E_{\text{x}}^{\text{DFA}}$ for a variety of mainstream DFAs, including the LDA, GGA, hybrid functional B3LYP, and range-separated functional MLDA. The detailed derivations are provided in Ref. [19]. For all the DFAs investigated, the SC contribution to exchange energy takes the following generic form:

$$\Delta E_{\text{x}}^{\text{DFA}} = \int d\mathbf{r} [\rho(\mathbf{r}) - g(\mathbf{r})] \theta_{\text{x}}^{\text{DFA}}(|\phi_f|^2; \mathbf{r}). \quad (3)$$

Here, the function $\theta_{\text{x}}^{\text{DFA}}(\mathbf{r})$ depends explicitly on $|\phi_f(\mathbf{r})|^2$. We emphasize that the form of $\theta_{\text{x}}^{\text{DFA}}$ is nonempirical (free of any fitted parameter) for the LDA, GGA, and B3LYP. By combining Eqs. (2) and (3), the XC energy associated with a scaled DFA (S-DFA) is thus

$$E_{\text{xc}}^{\text{S-DFA}} = E_{\text{xc}}^{\text{DFA}} + \Delta J + \Delta E_{\text{x}}^{\text{DFA}}. \quad (4)$$

This is the central result of this work. Specifically,

$$\theta_{\text{x}}^{\text{MLDA}}(\mathbf{r}) = -\frac{1}{2} \int d\mathbf{r}' \left[\frac{|\phi_f(\mathbf{r}')|^2 \text{erfc}(\mu |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \right] - \alpha_{\mu} C_{\text{x}} |\phi_f(\mathbf{r})|^{2/3}, \quad (5)$$

with $C_{\text{x}} = \frac{3}{4} (\frac{6}{\pi})^{1/3}$. We choose the semiempirical parameter $\alpha_{\mu} = 0.22222$ at $\mu = 0.5 \text{ bohr}^{-1}$ [19].

Although the self-consistent-field process inevitably alters the KS orbitals and modifies the scaling relation of each energy component, the scaling relation of total electronic energy is largely maintained. This is validated by the fact that a scaled DFA generally yields a much more straight energy curve than that by the original DFA [19], which also confirms that the SC significantly reduces the delocalization error associated with a convex DFA [4]. At

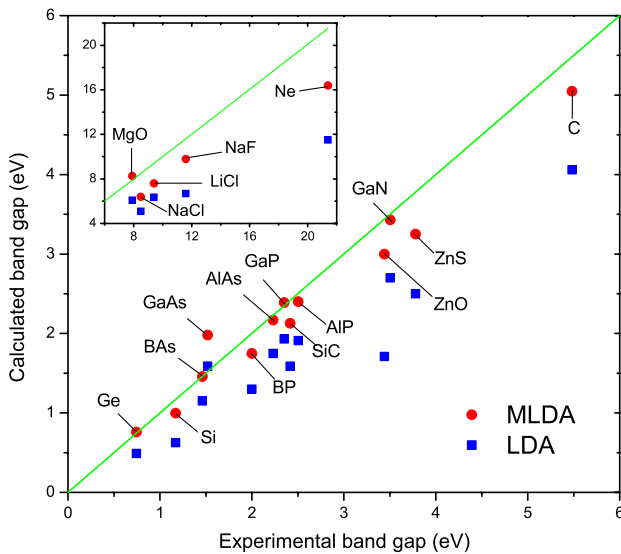


FIG. 1 (color online). Calculated versus experimental band gaps of a variety of nonmetallic solids. See Ref. [19] for details.

an integer point, the SC vanishes due to $\rho(\mathbf{r}) = g(\mathbf{r})$. Consequently, the S-DFA reproduces I , A , and $E_{\text{gap}}^{\text{int}}$ of the original DFA, while it improves significantly the prediction on ϵ_f and $E_{\text{gap}}^{\text{der}}$. We emphasize that virtually no extra computational cost is required for the evaluation of the SC-related quantities, and the SC method can be easily implemented in existing quantum chemistry software; see Sec. I E of Ref. [19] for details.

For molecules it is the vertical I (I_{ve}) and A (A_{ve}) that are relevant to ϵ_f and $E_{\text{gap}}^{\text{der}}$. Here, “vertical” means molecular geometry, and hence $\nu(\mathbf{r})$ do not change upon electron addition or depletion. Meanwhile, many experimental results are referred to as “adiabatic” values (I_{ad} and A_{ad}), where gaining or losing an electron is accompanied by geometry relaxation. Table I summarizes the band-gap-related quantities predicted by the LDA, B3LYP, MLDA, and their SC counterparts. The calculations cover atoms H–Ar, molecules in the G2-97 set, and representative solids in Fig. 1 [25]. Obviously, the LDA, B3LYP, and MLDA yield reasonable I and A , but they all give considerable errors on ϵ_f . In other words, $E_{\text{gap}}^{\text{int}}$ are obtained accurately, but $E_{\text{gap}}^{\text{der}}$ are severely underestimated. Inclusion of the SC significantly improves prediction of ϵ_f while preserving the accuracy of I and A . Among all the DFAs explored in Table I, the S-MLDA gives the most accurate $E_{\text{gap}}^{\text{der}}$ with consistent accuracy for systems of all sizes, i.e., from atoms and molecules to solids. Figure 2 compares ϵ_{HOMO} (ϵ_{LUMO}) with $-I_{\text{ve}}$ ($-A_{\text{ve}}$) for all the atoms and molecules studied, where the MLDA results display systematic discrepancies between pairs of quantities, which are apparently removed by using the S-MLDA.

The quantity of primary significance in the proposed SC method is the Fukui function. For solids, the apparent linearity condition is satisfied without the SC [4]. The periodic boundary condition requires $f(\mathbf{r}) = 0$, and thus the SC has no effect. In contrast, for finite systems $f(\mathbf{r}) \approx |\phi_f(\mathbf{r})|^2$, and the linearity condition is restored by the SC.

An important application of the SC is prediction of a size-dependent effect on band gaps of nanostructures, which has remained formidable in DFT. For instance, the quantitative relation between band gap and Si nanoparticle size has been studied extensively [27,28], as it highlights the significance of quantum confinement. The GW method [29] has been used to predict $E_{\text{gap}}^{\text{der}}$ through the quasiparticle orbital energies [30]. Reasonable $E_{\text{gap}}^{\text{int}}$ have been obtained by the DFT LDA for small size clusters but not for large ones [27]. $E_{\text{gap}}^{\text{der}}$ by the LDA suffer from a considerable delocalization error, which is expected to be removed by the SC.

We calculated $E_{\text{gap}}^{\text{der}}$ of H-passivated Si nanoparticles of various diameters (d). Computational details are provided in Ref. [19]. The $E_{\text{gap}}^{\text{der}}(d)$ obtained by the S-LDA correctly reproduces $E_{\text{gap}}^{\text{int}}$ by the LDA as reported in Ref. [27]; see Fig. 3. This confirms the efficacy of the SC on removing delocalization error at fractional occupation. Analogously,

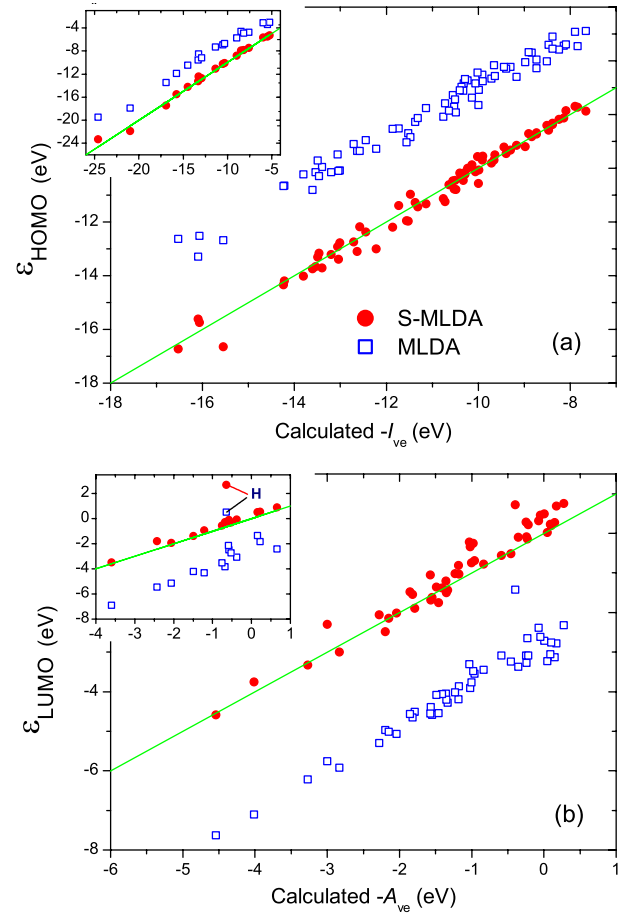


FIG. 2 (color online). (a) Calculated ϵ_{HOMO} versus $-I_{\text{ve}}$ for 70 molecules; (b) ϵ_{LUMO} versus $-A_{\text{ve}}$ for 47 molecules from the G2-97 set. Data for atoms H–Ar are shown in the insets, but without He, Ne, and Ar in the inset in (b). The solid line indicates $\epsilon_{\text{HOMO}} = -I_{\text{ve}}$ in (a) and $\epsilon_{\text{LUMO}} = -A_{\text{ve}}$ in (b).

the SC enlarges the MLDA gaps, and $E_{\text{gap}}^{\text{der}}$ by the S-MLDA agree well with the GW results [30]. Noting that the S-MLDA predicts more accurate $E_{\text{gap}}^{\text{der}}$ than the S-LDA for both SiH_4 ($d \rightarrow 0$) and bulk Si ($d \rightarrow \infty$) [19], we believe the S-MLDA prediction to be most reliable at any

TABLE I. Summary of MAEs in eV. Numbers of species calculated are given in parentheses. “S-” is short for scaled DFA. ϵ_{HOMO} (ϵ_{LUMO}) are compared to calculated I_{ve} (A_{ve}), and others are compared to experimental values [25,26].

	MAE	MLDA	S-	LDA	S-	B3LYP	S-
Atom	I (18)	0.16	0.16	0.30	0.30	0.20	0.20
	A (15)	0.25	0.25	0.27	0.27	0.12	0.12
	ϵ_{H} (18)	3.53	0.33	5.18	0.33	3.88	0.35
	ϵ_{L} (15)	2.47	0.54	3.33	0.65	2.28	0.67
Mole.	I_{ad} (70)	0.22	0.22	0.21	0.21	0.16	0.16
	A_{ad} (47)	0.25	0.25	0.24	0.23	0.13	0.13
	ϵ_{H} (70)	3.10	0.21	4.19	0.35	3.09	0.31
	ϵ_{L} (47)	2.78	0.27	3.66	0.34	2.59	0.39
Sol.	E_{gap} (18)	0.77	0.77	1.81	1.81	0.99	0.99

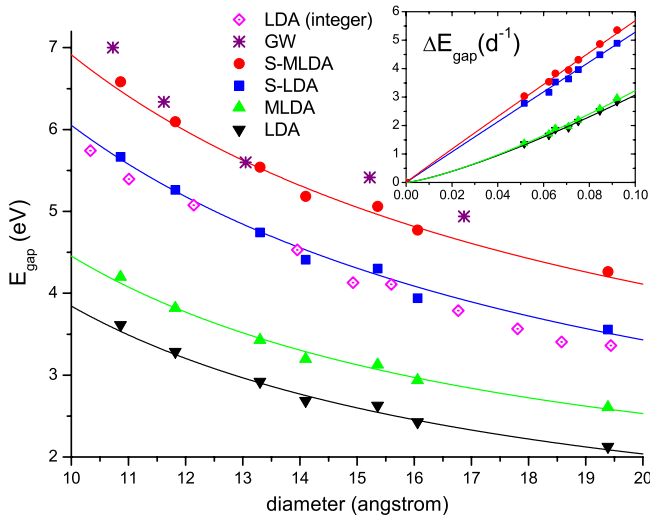


FIG. 3 (color online). $E_{\text{gap}}^{\text{der}}$ of H-passivated Si nanoparticles. The LDA and GW predicted $E_{\text{gap}}^{\text{int}}$ are extracted from Refs. [27,30]. The inset depicts $\Delta E_{\text{gap}}(d) = E_{\text{gap}}^{\text{der}}(d) - E_{\text{gap}}^{\text{der}}(\text{bulk})$. It is fitted to $\Delta E_{\text{gap}}(d) \approx a(d^{-1})^b$, with $b = 1.28, 0.99, 1.31$, and 0.98 for the LDA, S-LDA, MLDA, and S-MLDA, respectively.

finite d . As it also inherits from the MLDA the capability of predicting thermodynamic properties with similar or better accuracy than the GGA [19], the S-MLDA provides a useful tool to characterize quantitatively the size-dependent effects on physical properties of nanostructures. Stein *et al.* proposed a generalized KS method to improve $E_{\text{gap}}^{\text{der}}$ by optimizing the range-separation parameter μ for every system [31]. Our SC method is conceptually different, and no tuning of parameter is required. For the S-MLDA, the same value of μ is applied to all systems.

The significant improvement on band gap prediction across system sizes achieved by the SC affirms the understanding that it is useful to characterize DFT errors in the perspective of fractional charges [32]. The present SC method corrects the delocalization error in the energy derivatives for systems with integer electron numbers, by using the density matrix as a basic variable. We believe that this is a key step forward in the direction of correcting the delocalization error in the energy for systems with integer electron numbers, which is necessary to improve the prediction of thermodynamic properties in DFT.

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