Localization and delocalization errors in density functional theory and implications for band-gap prediction

Paula Mori-Sánchez, Aron J. Cohen, and Weitao Yang

Department of Chemistry, Duke University, Durham, North Carolina 27708

(Dated: February 5, 2008)

The band-gap problem and other systematic failures of approximate functionals are explained from an analysis of total energy for fractional charges. The deviation from the correct intrinsic linear behavior in finite systems leads to delocalization and localization errors in large or bulk systems. Functionals whose energy is convex for fractional charges such as LDA display an incorrect apparent linearity in the bulk limit, due to the delocalization error. Concave functionals also have an incorrect apparent linearity in the bulk calculation, due to the localization error and imposed symmetry. This resolves an important paradox and opens the possibility to obtain accurate band-gaps from DFT.

PACS numbers: 71.10.-w, 31.15.Ew, 71.15.Mb

Accurate band-gap prediction is critical for applications in condensed matter and nanotechnology. This unfortunately is not currently possible within the widely used density functional theory (DFT). The basic theory of the band-gap in DFT has been addressed [1,2] but confusion remains. In our recent work [3], it is shown possible to obtain the correct band-gap from DFT calculations and demonstrate the theory for finite systems.

The main challenge is in the approximate exchange-correlation functionals [4,5,6,7], which, despite the success in a wide range of applications, still suffer from systematic problems in describing charge-transfer processes, excitation energies in molecules, response properties in solids, electron transport and the band-gaps of semiconductors. Previous understanding has focused on self-interaction-error and the nature of the Kohn-Sham (KS) eigenvalues but recent work [3,8,9,10] has related self-interaction-error and the nature of the Kohn-Sham semiconductors. Previous understanding has focused on correlation functionals [4,5,6,7], which, despite the opportunities in condensed matter and nanotechnology. This uncertainty is not currently possible within the widely used density functional theory (DFT).

In this Letter, we will resolve a paradox on the apparent linearity in the bulk calculation, due to the localization error and imposed symmetry. This resolves an important paradox and opens the possibility to obtain accurate band-gaps from DFT.

Thus, for such an orbital functional, the KS eigenvalues from an optimized effective potential (OEP) [13] calculation are no longer the derivative of the energy expression. However, the derivatives can be exactly the eigenvalues in a generalized Kohn-Sham (GKS) calculation (e.g. Hartree-Fock calculations in the case of exact exchange) [3]:

\[ E^\text{der} = E^\text{KS} \]

We see that the second term on the right hand side of Eq. 4, which is labeled the derivative discontinuity \[ \Delta_{xc} \], is essentially the difference between an OEP and GKS calculation. However, it does not contain the physics of the error of the band-gap, as can clearly be seen from a consideration of the LDA or GGA band-gap.

The error in the band-gap calculation using approximate functionals is in the following

\[ E^{\text{integer}} = E^\text{der} + \Delta_{\text{straight}}, \]

thus

\[ E^{\text{gap}} = E^\text{gap} + \Delta. \]
where

\[ \Delta = \Delta_{xc} + \Delta_{\text{straight}}. \] (8)

Here \( \Delta_{\text{straight}} \), the difference between the gap from finite difference and the derivatives, accounts for the fact that an approximate functional may not have the correct straight line behavior between the integers. It is the consideration of this term, completely missing in the literature, that is the key in understanding the band-gap. We have seen that \( \Delta_{\text{straight}} \) has an important effect in the energy gap in molecules [1]. The focus of this Letter is to explore its implications for extended systems.

Now we present an important paradox for consideration of periodic or bulk systems: It has been argued in extended systems that the behavior of the total energy as a function of addition of an electron must be a straight line [1, 2], therefore \( \Delta = 0 \) for all functionals. How can it be opposite to the case of the finite systems [3, 8]? Furthermore, for LDA, \( \Delta_{xc} = 0 \), meaning that \( \Delta = 0 \). What is then the origin of the systematic error for LDA?

It is well known [1] that the calculation of semiconductors and wide gap insulators with a semi-local functional (such as LDA) has large systematic errors, underpredicting the band-gap by up to several eV.

We will resolve this apparent paradox by understanding more about the straight line behavior of energy functionals in solids.

The simplest periodic system to consider is a molecular crystal in the infinite lattice constant limit. We start with a monomer unit whose \( E(N) \) curve for different functionals is as in Fig. 1 the exact functional with correct straight line behavior, one with incorrect convex behavior for fractional charges (\( \delta N \)-convex) such as LDA, and another with incorrect concave behavior (\( \delta N \)-concave) such as HF theory. Next consider adding an electron to more than one monomer unit. If we first take the case of two monomer units, then we can see that adding an electron to a \( \delta N \)-convex functional leads to half an electron on each unit, as it is much lower than the energy of two monomers, with \( N \) and \( N + 1 \) electrons respectively. It is clear to see in this manner that with \( M \) monomer units

\[ ME(N + \frac{1}{M}) < (M - 1)E(N) + E(N + 1). \] (9)

As the number of units \( M \to \infty \), the added \( \delta \) electron delocalizes on to all the units such that the energy approaches the initial slope of the \( \delta N \)-convex monomer curve as in Figure 2:

\[ E(MN + \delta) = ME(N + \frac{\delta}{M}) \to ME(N) + \delta \frac{\partial E}{\partial N} \bigg|_{N+\delta}. \] (10)

In this way a functional like LDA, which is \( \delta N \)-convex for small molecules, will have an apparent linearity in large or periodic systems. It is, however, a qualitatively incorrect straight line, with the energy at the \( N + 1 \) integer point dictated by the fractional charge error of the functional. We can distinguish this from the correct behavior of the exact functional, which has intrinsic linearity with correct integer points for all \( M \), whereas \( \delta N \)-convex functionals are only linear in the limit \( M \to \infty \) with incorrect integer points. This is the delocalization error of \( \delta N \)-convex functionals.

The situation is reversed for \( \delta N \)-concave functionals, where the energy is always lower when the electron remains on one monomer unit, even as \( M \) increases. In fact the \( E \) vs. \( N \) curve is the same for all \( M \). Delocalization actually raises the energy, as the initial slope points
to above the integer points such that the inequality in Eq. (9) is reversed. For \( \delta N \)-concave functionals we will find \( \Delta_{\text{straight}} \neq 0 \) if we carry out an energy minimized calculation at \( N + 1 \) in an infinite system. This is the localization error in \( \delta N \)-concave functionals. However, if periodic symmetry is imposed in the calculation, then the additional electron is delocalized through the entire crystal as required by the translational symmetry, a straight line will be seen that follows the initial slope of the \( E \) vs. \( N \) curve. This delocalized state also has the energy of Eq. (10) which is a much higher energy, imposed by the symmetry. All the above arguments apply both to the addition of an electron and the addition of a hole (removal of electron).

In a periodic system, we see the maximum effects of the localization and delocalization error: for both \( \delta N \)-convex and \( \delta N \)-concave functionals, we will have the apparent linearity for the fractional charge, with the straight lines following the initial derivatives and leading to too low band-gap for \( \delta N \)-convex functionals and and too high band-gap for \( \delta N \)-concave functionals. This explains the errors in the band-gap prediction.

In a finite system, delocalization error increases with system size until the apparent linearity appears. But localization error stabilizes at certain system size. This also offers guidance on calculations of band-gap for finite systems: The approach to calculate the band-gap by explicit calculation of \( I \) and \( A \) from subtraction and addition of electron to finite neutral species, which works well with \( \delta N \)-convex functionals for small molecules [3], will not work for larger molecules, because localization error increases leading to the incorrect nature of the \( N - 1 \) and \( N + 1 \) points. However it may work for \( \delta N \)-concave functionals, which do not suffer from the apparent linearity problem (without translational symmetry) and may give meaningful integer points. This issue is also slightly clouded by the fact that HF theory may not give a reasonable energy for the localized electron or even the right amount of localization. Hence it will give an additional error to the integer points, but this has a a different physical basis.

The discussion up till now has focused on the energy differences and derivatives associated with the band-gap as it shows very clearly the basic physical biases of approximate functionals. However, these biases of the functionals have much wider implications. We can see the differing behavior of the two types of functionals: \( \delta N \)-convex (or LDA-type) functionals tend to delocalize electrons and \( \delta N \)-concave (or HF-type) functionals tend to localize electrons. So the nature of the electron density distribution is dictated by the functional rather than the underlying physics of the material. These are the delocalization and localization error of approximate functionals. An intrinsically linear functional does not suffer from these errors. The delocalization or localization error of approximate functionals are responsible for much of the deviation of calculated DFT properties from experimental results.

The idea of delocalization error introduced here is related to many-electron self-interaction error (SIE) [8] [10]. SIE has been blamed for a poor description of the band-gap, but without an understanding of the actual errors that it may introduce in to a particular calculation. We believe that the terms localization and delocalization error capture the physics of the problem in a more useful manner than self-interaction error.

The argument above is carried out in the infinite lattice constant limit but it is clear that same physical biases will be found at finite lattice constant in a normal periodic calculation. To illustrate the delocalization and localization errors we carry out a simple calculation on a one-dimensional system based on previous work [15] of...
H₂ polymer polarizability. We take a set of H₂ molecules that clearly shows the characteristic behavior of Fig. 1, a chain made up of 16 atoms, and repeat it with a 15 a.u. distance in between the units. The results in Fig. 3 have the same behavior as in Fig. 2, showing that the energy of a δN-concave functional (HF) remains the same, independent of the number of units, M. With LDA we see the convex behavior disappear as the delocalization error increase with M, and the E(N) curve becomes linear following the initial slope of the monomer unit. We can see that the point at the integer corresponding to the addition or subtraction is qualitatively wrong with a much too low energy. Even changing the distance between the units from 15 a.u. to 5 a.u. has no effect on Fig. 3.

Also in Fig. 4 we show a plot of the difference density (ρ(N + 1) − ρ(N)) for different sized units. We observe a clear difference between HF and LDA. HF localizes the extra electron to just one of the units, whereas LDA delocalizes the extra electron over all the units with a corresponding drop in energy. This clearly shows the delocalizing bias of LDA and the systematic error it can cause.

All these ideas tie in with the understanding of the band-gap originally from Kohn [16], which relates the band-gap to localization [17]. A systematic error in the band-gap implies a systematic error in describing localization, which is just what we find. There will also be a systematic qualitative error in the nature of the HOMO and LUMO orbitals and their corresponding eigenvalues for large molecules, as well as the conduction and valence bands for a crystal. These issues have widespread relevance in the calculation of many electronic properties of solids and large systems, as the delocalization error in δN-concave functionals like LDA affects large molecules and solids much more than small molecules.

The understanding given here also explains why TDLDA can be more successful for the calculation of small molecules and metals than for non-metallic infinite solids and polymers [14], where there is a basic problem in the description of the response of the density due to the delocalization error. It can also explain why Hartree-Fock and similar methods have problems with metallic systems due to the fact the functional localizes electrons and therefore opens a gap when the true nature should be to be delocalized with no gap at the Fermi-level.

To conclude, we have shown that the errors in the energy for fractional charges in finite systems leads to systematic errors at the integer points of larger systems. The addition of electrons or holes is poorly described by δN-convex functionals as they delocalize the added particle. This leads to errors in the initial slope as is seen by a band-gap calculation, but also means that the explicit calculation of I and A, for example in large cluster calculations, will suffer from the same error. Functionals which have opposite δN-concave behavior have the opposite tendency to localize electrons. This means that although there are problems using the initial slope we can still gain information from the explicit finite system calculation of I and A.

The understanding offered in this work explains the physical nature of the error in the band-gap from commonly used approximate functionals, and shows the implications of this error to the calculation of many other properties of solids, from optics to electron transport. A path forward is shown: by constructing functionals free from localization or delocalization error, one would be able to overcome most of the problems.

Financial support from the National Science Foundation is greatly appreciated. Discussions with Dr. San-Huang Ke and Dr. Xiangqian Hu have been helpful.

[1] J. P. Perdew and M. Levy, Phys. Rev. Lett. 51, 1884 (1983).
[2] L. J. Sham and M. Schlüter, Phys. Rev. Lett. 51, 1888 (1983).
[3] A. J. Cohen, P. Mori-Sánchez, and W. Yang (2007), arXiv:0708.3175v1 [cond-mat.mtrl-sci].
[4] A. D. Becke, Phys. Rev. A 38, 3098 (1988).
[5] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B 37, 785 (1988).
[6] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[7] A. D. Becke, J. Chem. Phys. 98, 5648 (1993).
[8] P. Mori-Sánchez, A. J. Cohen, and W. Yang, J. Chem. Phys. 125, 201102 (2006).
[9] A. J. Cohen, P. Mori-Sánchez, and W. Yang, J. Chem. Phys. 126, 191109 (2007).
[10] A. Ruzsinszky, J. P. Perdew, G. I. Csonka, I. O. A. Vydrov, and G. E. Scuseria, J. Chem. Phys. 126, 104102 (2006).
[11] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz Jr., Phys. Rev. Lett. 49, 1691 (1982).
[12] W. Yang, Y. Zhang, and P. W. Ayers, Phys. Rev. Lett. 84, 5172 (2000).
[13] J. D. Talman and W. F. Shadwick, Phys. Rev. A 14, 36 (1976).
[14] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. 74, 601 (2002).
[15] P. Mori-Sánchez, Q. Wu, and W. Yang, J. Chem. Phys. 119, 11001 (2003).
[16] W. Kohn, Phys. Rev. 133, A171 (1964).
[17] R. Resta and S. Sorella, Phys. Rev. Lett. 82, 370 (1999).