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Towards An Optimal Gradient-Dependent Energy Functional of the PZ-SIC Form

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Abstract
Results of Perdew–Zunger self-interaction corrected (PZ-SIC) density functional theory calculations of the atomization energy of 35 molecules are compared to those of high-level quantum chemistry calculations. While the PBE functional, which is commonly used in calculations of condensed matter, is known to predict on average too high atomization energy (overbinding of the molecules), the application of PZ-SIC gives a large overcorrection and leads to significant underestimation of the atomization energy. The exchange enhancement factor that is optimal for the generalized gradient approximation within the Kohn-Sham (KS) approach may not be optimal for the self-interaction corrected functional. The PBEsol functional, where the exchange enhancement factor was optimized for solids, gives poor results for molecules in KS but turns out to work better than PBE in PZ-SIC calculations. The exchange enhancement is weaker in PBEsol and the functional is closer to the local density approximation. Furthermore, the drop in the exchange enhancement factor for increasing reduced gradient in the PW91 functional gives more accurate results than the plateaued enhancement in the PBE functional. A step towards an optimal exchange enhancement factor for a gradient dependent functional of the PZ-SIC form is taken by constructing an exchange enhancement factor that mimics PBEsol for small values of the reduced gradient, and PW91 for large values. The average atomization energy is then in closer agreement with the high-level quantum chemistry calculations, but the variance is still large, the F₂ molecule being a notable outlier.

Keywords: density functional theory, self-interaction correction, exchange-correlation functional

1 Introduction
The Perdew–Zunger self-interaction correction (PZ-SIC) method is a way to correct for the spurious self-interaction error of electrons inherent in practical implementations of Kohn-Sham
(KS) density functional theory (DFT) [1]. The evaluation of the Coulomb interaction between the electrons in such functionals includes self-interaction terms which in the case of Hartree–Fock calculations are correctly canceled by exchange terms but are only partially canceled in DFT exchange-correlation (xc) functionals, for example, in the generalized gradient approximation (GGA). This self-interaction error generally results in an overestimation of the atomization energy of molecules, an underestimation of energy barriers for transitions as well as several other problems, such as overstabilization of delocalized states, underestimation of bandgaps in crystals, and erroneous ionization potentials (i.e., the orbital energy of the highest energy occupied orbital does not correspond to the IP).

The PZ-SIC functional is orbital density dependent and, thereby, is not a KS type functional. The energy obtained in a PZ-SIC calculations is not unitary invariant, i.e., different representations of the occupied orbital space give different values for the total energy of the system. The variational minimization of the energy of a PZ-SIC functional requires unitary optimization [3] as an inner loop in the self-consistency procedure. While such calculations are more demanding than the minimization of unitary invariant functionals, they give more meaningful results in that unique optimal orbitals are obtained, which typically are localized and in good correspondence with chemical intuition.

Recent calculations of atoms and molecules have shown that variational, self-consistent calculations using PZ-SIC need to be based on complex optimal orbitals [4, 5, 6]. Because of the orbital density dependence, there is need for full flexibility in the shape of each orbital, requiring the optimal orbitals to be complex-valued functions [4]. Requiring the orbitals to be real-valued imposes a restriction on the variational freedom of the system, resulting in systematically higher energies than in the same calculation with complex-valued orbitals, irrespective of the used basis set. The energy of single atoms is, furthermore, found to be too high compared to high-level quantum chemistry estimates in calculations using PZ-SIC with real-valued orbital and applied to, for example, the PBE [8] functional. The energy per electron is, however, close to the high-level estimates when complex optimal orbitals are used and the PZ-SIC then indeed improves the accuracy of the PBE functional [4, 6]. An even more dramatic illustration of this difference between real and complex optimal orbitals has been found when PZ-SIC is applied to the TPSS meta-GGA functional [6, 7]. For molecules, the restriction to real-valued orbitals in PZ-SIC calculations has been shown to result in incorrect geometry in some cases as well as less accurate results as compared with calculations using complex-valued optimal orbitals [5]. For example: The CH\(_3\) radical is correctly predicted to be planar when complex optimal orbitals are used, while it is non-planar when the PZ-SIC calculation is restricted to real orbitals [5].

While PZ-SIC calculations with the PBE functional gives excellent results for atoms, the bond energy in molecules, which tends to be overestimated in PBE calculations (the enthalpy of formation for the 233 molecules in the G3/99 database is on average overestimated by about 1 eV [9]) is overcorrected by PZ-SIC and gives too weak bonds [5]. It turns out that quite good estimates of bond energy, as well as band gaps of solids are obtained if the PZ-SIC terms are scaled by a factor of \(1/2\) during the self-consistent calculations when the PBE functional is used [10, 5]. However, this is not satisfactory in many respects; for example, the correct \(-1/r\) dependence of the effective potential is not obtained if such scaling is applied, and thus the method is not applicable to, e.g., studies of Rydberg excited states of molecules and clusters of molecules, an application for which PZ-SIC has turned out to be highly successful [12, 13, 14].

In functionals of the GGA form, the key ingredient is the exchange enhancement factor which is used to scale the exchange energy of the local density approximation. This is a one-dimensional function, \(F_x(s)\), of the magnitude of the reduced gradient, \(s = |\nabla n|/n^{4/3}\). In the limit of \(s \to 0\), \(F_x \to 1\), i.e., the local density approximation is obtained for the uniform electron
Fig. 1: Exchange enhancement factor, $F_x(s)$, for the PBE, PBEsol, PW91 and PWSIC functionals, as a function of the reduced gradient $s$. The PWSIC functional was constructed for this work and has similar asymptotic form as the PW91 functional, but is close to PBEsol for $s \leq 3.0$.

One of the early GGA functionals, PW91 [15], made use of a functional form of $F_x(s)$ that initially rises with increasing $s$ but then drops to zero, as shown in Fig. 1. In PBE, which is a simplified version of PW91 that has become commonly used, the function $F_x(s)$ is similar for small $s$ but approaches a non-zero value for large $s$, see Fig. 1. Despite their functional form, these two functionals typically give similar results for molecules and solids, illustrating that the region of large $s$ where the two functions differ appreciably is unimportant. This, however, is not the case when PZ-SIC is applied, as discussed in the Results section.

2 Calculations of atomization energy

We use here the all-electron ERKALE program [16, 17, 6] to test the accuracy of the calculated atomization energy for 35 molecules and make a comparison with results of high-level quantum chemistry calculations of chemical accuracy [11]. The atomization energy of the following molecules was calculated: H$_2$, BeF$_2$, BeCl$_2$, BH, BH$_3$, B$_2$H$_6$, BF, CH$_2$ (singlet), CH$_2$ (triplet), C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, NH$_2$, NH$_3$, N$_2$, H$_2$O, O$_2$, HF, F$_2$, AlH, AIH$_3$, AlF, AlCl, SiH, SiH$_4$, SiO, SiF, PH$_3$, P$_2$, H$_2$S, SO, SO$_2$, ClO, ClF and Cl$_2$. The calculations are variational and self-consistent, in that we minimize the energy of the PZ-SIC energy functional with the chosen GGA expression for the functional. The form of the orbitals is determined from the variational minimization of the energy, rather than the use of an approximate scheme such as Foster–Boys or Wannier orbitals. The complex optimal orbitals are formed here by linear combination of complex canonical orbitals. In many cases it is sufficient to form complex optimal orbitals from real canonical orbitals, but there are examples where this has proved to be less than optimal, the acrylic acid molecule being one example [6, 7].
We compare the results obtained with three commonly used generalized-gradient approximation (GGA) functionals, as well as a new functional, PWSIC, which has an exchange enhancement function constructed for use with PZ-SIC. It has the same asymptotic form as the PW91 functional, but similar values as PBEsol [18] for $s \leq 3.0$. The exchange enhancement factor functions for the PBE, PBEsol, PW91 and PWSIC functionals are shown in Fig. 1.

3 Results

The results of the atomization energy calculations of the 35 molecules are shown in Fig. 2. The mean error as well as root-mean-square error calculated for this set is shown, as well as the values obtained for each molecule. The value have not been scaled with the number of atoms or bonds, so larger errors are expected for the larger molecules. It is clear from these results that the values obtained using the PZ-SIC method are strongly dependent on the choice of the functional. Apart from the difference in the exchange enhancement function we note that there is also a small difference in the correlation functional in PBE and PW91.

As mentioned in the introduction and as already pointed out previously [5], the PZ-SIC applied to PBE overcorrects and changes the overbinding of the molecules in PBE to an underbinding of ca. 1/2 eV on average. Only three of the molecules have too large atomization energy, the rest of the molecules being too weakly bound. However, we point out that the en-
ergy of the atoms is accurately reproduced [4, 6], so the problem must lie mainly in the energy of the molecules. The outliers there are the much too weakly bound F₂ and SO₂ molecules. The largest deviation in KS, with too strong binding, is the O₂ molecule (overbound by about 1 eV with PBE, but becomes underbound by -0.8 eV when PZ-SIC is applied).

PBEsol is a functional of the PBE form, but with parameters tailored to give more accurate results for solids. It has an exchange enhancement function that is closer to the local density approximation, and as a result works worse than PBE for molecules and gives even stronger bonding. While PBE strikes some balance between opposing tendencies for molecules and solids, as well as for energetics and structure, PBEsol is especially tailored to solids and works poorly for molecules. However, when PZ-SIC is applied to PBEsol the energy of atoms is in even better agreement with high-level calculations than with PZ-SIC applied to PBE [6]. PZ-SIC apparently builds in some of the gradient dependence that is required, and as a result a smaller rise in the exchange enhancement function is necessary. This holds also for molecules and PZ-SIC applied to PBEsol shows remarkably good agreement with the high-level quantum chemistry calculations, as can be seen in Fig. 2.

While the PW91 functional typically gives nearly the same results as PBE for both molecules and solids within the KS approach, the results of applying PZ-SIC are significantly different, see Fig. 2. The main reason for this is the drop in the exchange enhancement function for large values of the reduced gradient in PW91. The reduced gradient can reach large values on nodal surfaces, where the density is small while the gradient is non-zero. Since the energy functional is evaluated for each orbital density in PZ-SIC calculations, this means that the functional accumulates significant contributions from the region of large s, while in KS calculations the energy functional is evaluated only for the total electron density which gives a more limited range of values for s. The drop to zero in $F_\alpha(s)$ for large s in PW91, therefore, gives better results than the near constant value of $F_\alpha(s)$ for large s in PBE. A notable improvement can, in particular, be seen in the atomization energy of the outliers, F₂ and SO₂.

4 Conclusion

In a small step towards developing an optimal GGA functional for PZ-SIC calculations, we have generated an exchange functional with the same parametric form as PW91 refitted to match PBEsol at small values of the reduced density gradient. The calculated atomization energy for a set of molecules using this new functional has nearly zero mean deviation and is an improvement over the common xc functionals, but the RMS deviation is still large. Clearly, the use of PZ-SIC calls for a re-evaluation of the optimal functional. The optimal exchange enhancement factor for use with PZ-SIC applied to a GGA functional remains to be developed, as well as analysis of the optimal choice of correlation functional.

This work is underway where, for example, the correlation functional form of Lee, Yang and Parr (LYP) [19] is a promising candidate for use with PZ-SIC. Furthermore, the correlation energy formula by Colle and Salvetti [20], of which LYP is based on, is being revisited with orbital dependence in mind. It will be important in the ongoing development of the optimal xc functional to study various other properties, such as atomic energy, molecular structures and ionization energy, in addition to atomization energy. However, it is clear that by expanding the functional form to include explicit orbital density dependence as in PZ-SIC new avenues for energy functional development are opened.
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