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How well can density functional theory and pair-density functional theory predict the correct atomic charges for dissociation and accurate dissociation energetics of ionic bonds?

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| Journal: | <i>Physical Chemistry Chemical Physics</i> |
| Manuscript ID | CP-ART-07-2018-004280 |
| Article Type: | Paper |
| Date Submitted by the Author: | 06-Jul-2018 |
| Complete List of Authors: | Bao, Junwei; University of Minnesota, Chemistry Truhlar, Donald; Department of Chemistry, University of Minnesota Verma, Pragya; University of Minnesota College of Science and Engineering, |
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How well can density functional theory and pair-density functional theory predict the correct atomic charges for dissociation and accurate dissociation energetics of ionic bonds?

Received 00th Month 2018,
Accepted 00th Month 2018

DOI: 10.1039/x0xx00000x

Junwei Lucas Bao, Pragya Verma and Donald G. Truhlar*^a

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The accuracy of density functional theory (DFT) is often judged by predicted dissociation energies, but one should also consider charge densities as illustrated here for dissociation of heteronuclear diatomic molecules, including ionic bonds for which local density functionals yield erroneous results. Some hybrid density functionals with 100% exact exchange in Kohn-Sham DFT and the local functionals in multiconfiguration pair-density functional theory give relatively accurate dissociation energies for NaCl, and they correctly yield uncharged dissociated atoms for both cases.

1. Introduction

Kohn-Sham density functional theory^{1,2} (KS-DFT) has been an indispensable tool for understanding, simulating, and predicting chemical phenomena, but it still has shortcomings due to the approximate nature of available density functionals. In KS-DFT, local exchange-correlation (xc) functionals (those for which the energy density at a point depends only on local quantities at that point, like α and β spin densities, their derivatives, and local kinetic energy densities) are known to have delocalization error,³ that is, they sometimes predict that electronic charge distributions are more delocalized than they really are, and this can lead to errors in charge transfer probabilities, transition metal bond energies and spin states, electronic excitation energies, band gaps and band alignment, localization of small polarons, and many other properties;^{4,5,6} therefore the issue has broad implications. These problems can usually be ameliorated by adding a portion of nonlocal Hartree-Fock (HF) exchange to the functional, yielding so called hybrid functionals, but the portion to be added depends on the system and the property, and HF exchange does not completely eliminate the problem. Delocalization error can be characterized by the delocalization of charge in a He_N^+ cluster with widely separated nuclei,³ for which most KS-DFT functionals incorrectly yield a delocalized hole with a lower

ionization energy than a single He atom.⁷ In the present work, we consider another well-defined example of delocalization error, namely the charge distribution in the dissociation limit of some ionic bonds in neutral heteronuclear molecules, for which NaCl serves as a prototypical example; NaCl (like all other diatomics) dissociates to neutral atoms, but it is well known that many density functionals predict delocalized molecular orbitals for dissociated bonds and lead to fractional charges on the two atoms.^{8,9} In other words, they incorrectly predict that putting a fraction of an electron on each center is lower in energy than localizing each electron; the latter would lead to whole number of electrons on each center. Furthermore, even if one gets an integer number of electrons on each center the question arises whether the lowest energy solution corresponds to $\text{Na}^+ + \text{Cl}^-$ or $\text{Na} + \text{Cl}$.

Here we examine two possible avenues to correct this problem. One is to use improved density functionals in KS-DFT. The other is to use multiconfiguration pair-density functional theory^{10,11} (MC-PDFT) in which the energy is calculated based on a multiconfiguration wave function and an on-top functional based on density and pair density, rather than on the noninteracting-electron Slater determinant and the exchange–correlation functional based on spin densities, as used in KS-DFT.

One term in the energy in both KS-DFT and MC-PDFT is the classical Coulomb energy of the electronic charge distribution, in which the entire electronic charge distribution interacts with itself so that effectively an electron is incorrectly interacting with its own density; this is called one-electron self-interaction error (1eSIE), and it can only be fully corrected by a nonlocal functional. Nonlocal exchange can lessen delocalization error by minimizing 1eSIE,^{12,13} but, although 1eSIE certainly contributes to delocalization error, delocalization error can occur even in the absence of 1eSIE.³ In systems with more than one electron, 1eSIE is inseparable from other sources of errors. Furthermore, although wave function theory (WFT) with properly antisymmetrized wave functions has no 1eSIE, in some cases where the errors are conventionally attributed to 1eSIE, multiconfiguration pair-density functional theory^{10,11}

^a Department of Chemistry, Chemical Theory Center, and Minnesota Supercomputing Institute, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455-0431, United States. Email: truhlar@umn.edu.

(MC-PDFT) with local functionals predicts a smaller error than some 1eSIE-free wave function methods. With KS-DFT, however, it appears that one needs nonlocal exchange to get such good results.¹⁴ This situation motivates the quest for a better understanding of delocalization error in density functional theories.

Delocalization error is often studied in homonuclear systems such as the He_N^+ cluster^{3,7} and homonuclear diatomic cations (e.g., H_2^+ and He_2^+).^{15,16,17,18} The discussion of these systems can be complicated by point group symmetry, and one sometimes gets significantly different results by introducing a small perturbation that breaks the symmetry but has little other effect (this is especially true if one tries to enforce symmetry on the Slater determinant). In most practical applications and even for molecular dynamics of small systems with symmetric equilibrium geometries, real systems spend all or most of their time in asymmetric geometries. We believe that one can achieve a better understanding of systems of practical interest by decoupling the spatial symmetry issue from the tests of delocalization and self-interaction errors, and this can be done most easily by studying asymmetric heteronuclear systems. Here, we propose to use the dissociation of asymmetric molecules, in particular NaCl, AlO, LiH, and HF to examine the consequences of delocalization error in density-functional theories.

In analysing the problem, we calculate the bond energy and the charges on dissociated atoms by setting the distance between the atoms to 10 Å, at which point the bond is for all practical purposes dissociated; and we calculate partial atomic charges at any internuclear distance by dividing the calculated dipole moment at that distance by the distance. We define q as the partial atomic charge on the atom with smaller electronegativity (for instance, for NaCl the charge on Na is q and the charge on Cl is then $-q$).

2. Computational details

For all the calculations, the aug-cc-pVQZ basis is used for H, Li, O, F, Na,¹⁹ and Al,²⁰ and the aug-cc-pV(Q+d)Z basis is used for Cl.²¹ All the calculations are single-point calculations, and the equilibrium bond length is 2.379 Å for NaCl, 0.915 Å for HF, 1.592 Å for LiH, and 1.626 Å for AlO (which has a $^2\Sigma$ state²² as the ground state), as obtained with the M06-L density functional. Both localized and delocalized initial orbital guesses were tried and we also varied our initial guesses that are generated from other functionals for self-consistent-field (SCF) calculations in order to obtain the variationally lowest-energy solutions.

For NaCl, HF, LiH, and AlO, unrestricted coupled-cluster theory with single excitations, double excitations, and quasi-perturbative triple excitations (UCCSD(T))²³ from an unrestricted Hartree-Fock²⁴ (UHF) wave function with the above-mentioned quadruple-zeta basis set is used for computing the equilibrium dissociation energy. We have checked that UCCSD(T) is size-extensive in that the computed energy for the supermolecule A...B at 10 Å is equal to the summation of the separately computed energy for A and for B.

For AlO, the W2X theory,²⁵ which is an approximation to CCSD(T)/CBS, and W3X-L theory,²⁵ which starts with W2X and adds post-CCSD(T) contributions up to the CCSDT(Q) level, are also used to compute its dissociation energy. Because of the implementation for doublets in *Molpro*,²⁶ the unrestricted coupled-cluster calculation is carried out based on a restricted open-shell Hartree-Fock (ROHF) reference wave function, and this yields ROHF-UCCSD(T).

We performed KS-DFT calculations for all four molecules and multireference calculations for NaCl and AlO. The reference wave function for multireference calculations is complete active space SCF (CASSCF^{27,28}). For CASSCF calculations, following the nominal correlated participating orbitals (nom-CPO) scheme,^{29,51,30} the active space used for singlet NaCl is (2e, 2o) which includes σ and σ^* orbitals, and for doublet AlO it is (7e, 8o) which includes one σ , one σ^* , two π , two π^* , one n and one n' orbitals. Complete active space second-order perturbation theory was calculated both without (CASPT2-0³¹) and with (CASPT2³²) the empirical IPEA shift (0.25 a.u.³²). MC-PDFT calculations are performed with translated¹⁰ (prefix t) and fully translated³³ (prefix ft) functionals. Restricted Hartree-Fock³⁴ (RHF), UHF, unrestricted Møller-Plesset 2nd-order perturbation theory (UMP2)³⁵, UCCSD(T), and KS-DFT calculations are performed with locally modified *Gaussian 09*^{36,37} or *Gaussian 16*³⁸ software. CASSCF, CASPT2-0, CASPT2, and MC-PDFT calculations are performed with *Molcas 8.1*³⁹ software. W2X and W3X-L calculations are performed with the *Molpro*²⁶ and *MRCC*⁴⁰ codes.

Unlike some previous tests of the theory, in the present study all KS-DFT and UHF calculations are allowed to be spin-polarized, i.e., during the SCF iterations the α and β spin-orbitals are variationally optimized to be different if this lowers the computed energy (which is a standard way of performing practical KS-DFT calculations on open-shell systems and is a formalism²⁴ widely used in WFT as well); the spatial symmetry or asymmetry of orbitals is also variationally optimized. MC-PDFT always has the correct spin symmetry, and for the present applications the variationally best orbitals turn out to have $C_{\infty v}$ point group symmetry. In contrast, the Slater determinants of some spin-polarized KS-DFT calculations, even when they have the correct charge at large internuclear distances, have the wrong spin symmetry and the variationally optimized orbitals possibly have broken spatial symmetry. For instance, for LC-BLYP functional, the solution for NaCl at 10 Å is significantly spin contaminated with spin $\langle S^2 \rangle = 1.00$, which corresponds to a 50:50 mixture of singlet and triplet. This is a well-known phenomenon – the same as one finds with spin-polarized KS-DFT for dissociation of H_2 .

In addition to testing density functionals for the charge on dissociation products, we test them for the equilibrium bond dissociation energy (D_e) and the reference value for testing was obtained as follows. The UCCSD(T) computed D_e for NaCl is 97.8 kcal (all energies are per mole), which agrees very well with the literature value of 98.0 kcal as obtained by combining the zero-point vibrational energy of 0.52 kcal⁴¹ with the ground-state D_0 dissociation energy of 97.5 kcal.⁴² The UCCSD(T) computed D_e for HF is 140.9 kcal, which agrees very

well with the experimental value 141.2 kcal;⁴³ and the computed D_e for LiH is 57.4 kcal, which is in good agreement with the experimental value 58.0 kcal.⁴⁴ For NaCl, HF, and LiH, the experimental values are used as reference values for computing errors in D_e .

For AlO, the D_e computed by the W2X method is 122.9 kcal and by the W3X-L method is 125.6 kcal. This difference indicates large multireference effects. The experimentally measured D_e for AlO ($^2\Sigma$ state) varies quite significantly among different studies: Tyte's measurements give a value of 104.7 kcal;⁴⁵ Murthy et al.⁴⁶ summarized 17 previous measurements of which the D_e values (which we computed by adding the reported D_0 values to a ZPE of 1.39 kcal calculated from NIST data⁴⁷) range from 22.4 kcal to 146.4 kcal; their own reported D_e value is 95.7 kcal. Patrascu and co-workers reported a value of 112.8 kcal.⁴⁸ The 0 K atomization energy reported by NIST is 121.29 kcal, which corresponds to a D_e of 122.7 kcal. In this work, we use the W3X-L dissociation energy as the benchmark value for AlO.

3. Results and Discussion

3.1 NaCl dissociation energy and the charge at the dissociation limit

Consider first the application to NaCl. At the equilibrium internuclear distance, q is positive, while at the dissociation limit it should be zero. However, with KS-DFT, instead of predicting dissociation to the open-shell singlet consisting of two doublet neutral atoms, local functionals and some hybrid functionals give nonzero atomic charges at the dissociation limit. For instance, the PBE0 functional predicts that the highest-energy occupied β molecular orbital (the " β -HOMO") is delocalized over the separated centers, while the α -HOMO is localized as a Cl $p\sigma$ orbital; all the other MOs are localized on either Na or Cl. Similarly, the BLYP functional, predicts the β -HOMO is delocalized over the two centers, and all the other MOs are localized, including the α -HOMO and β -HOMO-1, which are localized on Cl. The delocalization error is characterized by the charge on dissociated atoms (at 10 Å), which is shown in Table 1.

The table shows that WFT (which is self-interaction-free but which can suffer from over-localization of charge if applied at too low of a level of theory) gives whole numbers of electrons on neutral atoms, and the table shows that except for RHF, the WFT methods all produce zero atomic charge at the dissociation limit. The errors (in kcal) in D_e are -28.4 (UHF), -2.1 (RHF), -4.8 (UMP2), -19.4 (CASSCF), -0.7 (CASPT2-0), and 1.1 (CASPT2).

Table 1 shows that in KS-DFT calculations, none of the local functionals nor any of the hybrid functionals with less than 100% nonlocal exchange produces the correct zero atomic charge on dissociated atoms. Functionals that give nonzero charge even at large internuclear separation have unphysical electrostatic attraction at 10 Å, which can cause a cancellation of errors that leads to small errors in the dissociation energy in Table 1; sometimes this kind of outcome is called "obtaining the right answer for the wrong reason".

At 10 Å, the KS-DFT functionals that are able to give the correct atomic charge and dissociation energy are LC-BLYP (with a bond energy error of -1.6 kcal), LC- ω PBE (-3.3 kcal error), HFLYP (-7.0 kcal error), and M06-HF (-7.3 kcal error). All of these functionals have 100% nonlocal exchange at long range. However, density functionals with a small amount of nonlocal exchange are favored for many purposes because high nonlocal exchange introduces static correlation error,⁴⁹ and thus functionals with high nonlocal exchange often give poor results for strongly correlated systems, which are systems with near-degeneracy correlation effects; this includes many transition metal systems.^{50,51}

The MC-PDFT calculations all involve local functionals (but with self-interaction-free density^{10,14}), and they all give neutral atoms at 10 Å. The average error in D_e for the MC-PDFT calculations is -4.2 kcal, as compared to -23.4 kcal for KS-DFT with local functionals and -11.3 kcal with hybrid functionals. The error of MC-PDFT with the local tPBE and ftPBE functionals are only -3.5 and -1.2 kcal, respectively, which are significantly better than the errors given by KS-DFT with the parent PBE local functional (-29.4 kcal), and even the PBE0 hybrid version of this functional (-20.5 kcal). The errors for MC-PDFT are also much less than that for the popular B3LYP hybrid functional (-24.1 kcal).

Table 1. Error (kcal) of the computed NaCl bond dissociation energy and Na charge at the dissociation limit

| Method | Type ^a | Ref. ^a | X^b | Error | q |
|------------------|-------------------|-------------------|-------------|-------|------|
| UHF | WFT | 24 | NA | -28.4 | 0.00 |
| RHF | WFT | 34 | NA | -2.1 | 1.00 |
| UMP2 | WFT | 35 | NA | -4.8 | 0.00 |
| CASSCF | WFT | 27,28 | NA | -19.4 | 0.00 |
| CASPT2-0 | WFT | 31 | NA | -0.7 | 0.00 |
| CASPT2 | WFT | 32 | NA | 1.1 | 0.00 |
| UCCSD(T) | WFT | 23 | NA | -0.2 | 0.00 |
| BLYP | KS-DFT | 52,53 | 0 | -32.2 | 0.45 |
| PBE | KS-DFT | 54 | 0 | -29.4 | 0.46 |
| revPBE | KS-DFT | 55 | 0 | -31.5 | 0.46 |
| M06-L | KS-DFT | 56 | 0 | -15.6 | 0.61 |
| revM06-L | KS-DFT | 57 | 0 | -15.8 | 0.50 |
| MN12-L | KS-DFT | 58 | 0 | -22.2 | 0.52 |
| MN15-L | KS-DFT | 59 | 0 | -23.1 | 0.52 |
| HLE17 | KS-DFT | 60 | 0 | -17.4 | 0.49 |
| B3LYP | KS-DFT | 52,61 | 20 | -24.1 | 0.45 |
| MN12-SX | KS-DFT | 62 | 25-0 | -21.7 | 0.54 |
| HSE06 | KS-DFT | 63 | 25-0 | -22.8 | 0.45 |
| PBE0 | KS-DFT | 64 | 25 | -20.5 | 0.44 |
| M06 | KS-DFT | 65 | 27 | -12.6 | 0.68 |
| MN15 | KS-DFT | 66 | 44 | -13.1 | 0.48 |
| BHandH | KS-DFT | 67 | 50 | -9.6 | 0.40 |
| M08-HX | KS-DFT | 68 | 52.2 | -12.7 | 0.48 |
| M06-2X | KS-DFT | 65 | 54 | -3.2 | 0.75 |
| CAM-B3LYP | KS-DFT | 69 | 19-65 | -11.6 | 0.40 |
| HISS | KS-DFT | 70 | 0-100-0 | -19.5 | 0.44 |
| LC- ω PBE | KS-DFT | 71 | 0-100 | -3.3 | 0.00 |
| LC-BLYP | KS-DFT | 72 | 0-100 | -1.6 | 0.00 |
| ω B97X | KS-DFT | 73 | 15.7706-100 | -0.9 | 0.99 |
| M11 | KS-DFT | 74 | 42.8-100 | -0.3 | 0.91 |
| HFLYP | KS-DFT | 24,52 | 100 | -7.0 | 0.00 |
| M06-HF | KS-DFT | 75 | 100 | -7.3 | 0.06 |
| tPBE | MC-PDFT | 10 | 0 | -3.5 | 0.00 |
| trevPBE | MC-PDFT | 76 | 0 | -5.3 | 0.00 |
| tBLYP | MC-PDFT | 10 | 0 | -7.5 | 0.00 |
| ftPBE | MC-PDFT | 33 | 0 | -1.2 | 0.00 |
| ftrevPBE | MC-PDFT | 76 | 0 | -3.3 | 0.00 |
| ftBLYP | MC-PDFT | 33 | 0 | -4.6 | 0.00 |

^a type of method and reference for method

^b percentage of nonlocal exchange in the functional (NA = not applicable); in some cases, there is a range depending on interelectronic distance

The question arises of whether the success of MC-PDFT results simply from using a self-interaction-free density. To answer this, we performed post-SCF KS-DFT energy calculations using the PBE, M06-L, and M06 functionals with spin-polarized HFLYP densities. For PBE, the absolute error in the dissociation energy is decreased by 14.2 kcal. But for M06-L and M06, the absolute error in the dissociation energy is respectively increased by 9.4 and 4.2 kcal. Therefore, it is not enough to simply use a density free from 1eSIE.

For UHF, UMP2, the CAS methods, MC-PDFT, and the hybrid KS-DFT methods that yield $q = 0$, one would obtain the same D_e if one did the calculations on separated atoms and added the energies. Clearly, though, this is not true for methods that yield non-integer q . Therefore, it is important that we calculated q and D_e at a finite distance to ascertain the limit to which the charge and potential curve are tending as the internuclear distance is increased over the chemically relevant range of distances, that is, to actually test the calculation of the potential energy curve. However, because of the delocalization error, even at 10 Å, the energies obtained with functionals with nonzero q have a non-negligible classical Coulomb attraction, and this affects the calculated dissociation energy at this distance. Therefore, for such systems, the computed dissociation energy of NaCl depends on the choice of interatomic distance used for the separated atoms; this dependence is itself unphysical because 10 Å is large enough that the interatomic interaction is negligible in the real system. As an example, with the M11 functional, at 10 Å the dissociation energy is only 0.3 kcal lower than the reference value and charge on Na is (unphysically) 0.91, but at 20 Å the dissociation energy is 4.3 kcal higher than the reference value, and the charge on Na is 0. However, the failure at 10 Å is an indication that the potential curve calculated with this functional is dissociating to the wrong limit at chemically relevant distances and that the functional fails the delocalization test; in a real dynamics calculation, one cannot simply avoid the problem by doing dynamics only at distances of 20 Å or more, where the delocalization error is not noticeable (for some functionals). For this reason, although there is some arbitrariness in the precise choice of 10 Å as a comparison distance, we believe it is more relevant than using an even larger distance.

3.2 NaCl dissociation curves and the charge along dissociation

Dissociation curves for PBE, tPBE, and the UCCSD(T) coupled cluster method are shown in Figure 1, in which each curve is relative to zero at its minimum at 2.4 Å. The tPBE curve agrees very well with the UCCSD(T) curve, but the PBE curve significantly underestimates the potential curve of UCCSD(T) due to delocalization error, from which tPBE does not suffer.

As one increases the Na-Cl distance, one expects q to decrease suddenly around the ionic-covalent crossing, which can be estimated to be at 9.5 Å for NaCl.⁷⁷ CASSCF is expected to quantitatively underestimate the distance at which the charge transfer occurs,^{78,79} and therefore the present tPBE calculations, which use the CASSCF density, will also

underestimate the position; this is confirmed in Fig. 2, which shows the decrease of q occurs at 6.6 Å for tPBE. Although the switch position is not quantitatively accurate, tPBE predicts a reasonably accurate dissociation energy for the right reason, i.e., as the energy of neutral atoms minus the energy of the molecule. For UHF, the switch occurs even earlier at 5.6 Å. For PBE, Fig. 2 does not show a switch; the PBE charge on Na starts decreasing gradually at 3.2 Å (where the charge is 0.77), and it approaches 0.46 charge at the dissociation limit. This is typical of the results obtained with KS-DFT local functionals or hybrid functionals with less than 100% nonlocal exchange.

As mentioned earlier, a reasonable density and good dissociation energy can be simultaneously obtained in KS-DFT by the LC-BLYP functional. For LC-BLYP, the switch between ionic and covalent character takes place at 9.4 Å, in good agreement with the accurate switch position at 9.5 Å. For M11, there is a switch at 12.4 Å, which is 3 Å too large.

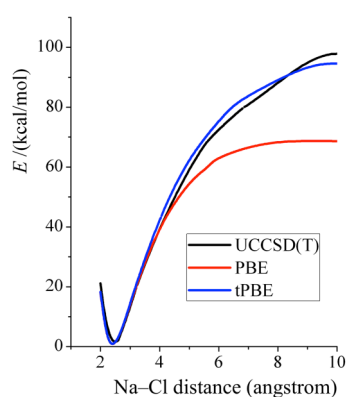


Figure 1. Potential energy curves as functions of the Na-Cl distance (Å).

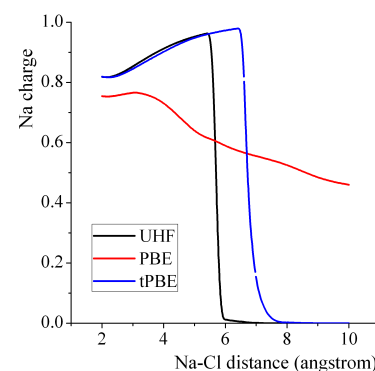


Figure 2. Na charge as a function of Na-Cl distance (Å).

3.3 Dissociation energy of other ionic or partially ionic bonds and their charges at the dissociation limit

Here we briefly examine the issue of producing the wrong charge at the dissociation limit due to the delocalization error in other ionic bonds. For many diatomics, the delocalization error is not well exposed by the kind of test that we considered here; for some molecules even local functionals can yield the correct zero charge in the dissociation limit. For

instance, for lithium hydride (LiH) at 10 Å, the variationally lowest-energy solution obtained with PBE gives zero charge on Li, while its dissociation energy (53.8 kcal) is only 3.6 kcal lower than the UCCSD(T) value and is 4.2 kcal lower than the experimental value; we have also checked other functionals, and their variationally lowest-energy solutions all dissociate to zero charge at the dissociation limit. For hydrogen fluoride (HF) at 10 Å, all functionals tested here dissociate correctly to zero charge except for BLYP, which gives a small charge on H (only 0.09), but which has a dissociation energy of 139.0 kcal which is only 2.2 kcal from the experimental value of 141.2 kcal.

In order to further examine the generality of the success of the density functional methods that produced the correct zero charges at 10 Å in the NaCl test, we here apply them – along with a few other functionals for comparison – to AIO, for which we found that at least some of the local functionals yield nonzero atomic charge at the dissociation limit. The additional density functional and pair-density functional tests we performed are summarized in Table 2.

Table 2. Error (kcal) of the computed bond dissociation energy and atomic charge at the dissociation limit (10 Å) for AIO

| Method | Error | q |
|------------------|-------|------|
| UHF | -70.0 | 0.00 |
| ROHF | -73.3 | 0.00 |
| CASSCF | -14.1 | 0.00 |
| CASPT2 | 2.7 | 0.00 |
| UHF-UCCSD(T) | -7.7 | 0.00 |
| W2X | -2.8 | 0.00 |
| BLYP | -9.2 | 0.29 |
| PBE | -4.8 | 0.26 |
| revPBE | -10.9 | 0.25 |
| B3LYP | -9.3 | 0.18 |
| PBE0 | -10.0 | 0.09 |
| MN15 | -0.6 | 0.00 |
| M06-2X | -5.5 | 0.00 |
| LC- ω PBE | -7.5 | 0.00 |
| LC-BLYP | -1.4 | 0.00 |
| HFLYP | -36.3 | 0.00 |
| M06-HF | -8.2 | 0.00 |
| tPBE | -5.2 | 0.00 |
| trevPBE | -10.5 | 0.00 |
| tBLYP | -9.5 | 0.00 |
| ftPBE | -8.4 | 0.00 |
| ftrevPBE | -14.8 | 0.00 |
| ftBLYP | -11.3 | 0.00 |

For AIO, we find that MN15 and LC-BLYP dissociate correctly and have only small errors in the dissociation energy, and the other hybrid functionals tested here (except for PBE0, which gives an 0.09 charge, and B3LYP, which gives 0.18 charge) also dissociate correctly. As compared to our benchmark, MN15 gives the smallest error (-0.6 kcal) among the functionals we tested for AIO. BLYP underestimates the bond dissociation energy, and it gives an Al charge of 0.29 at 10 Å, which causes unphysical electrostatic attraction that lowers its computed dissociation energy by cancellation of errors. On the other hand, MC-PDFT gives zero charge at 10 Å, although the computed bond energies are not as accurate as one might hope for. The tPBE pair-density functional, which has usually been the default choice in previous MC-PDFT work, gives an error in the bond energy of only -5.2 kcal and it yields the correct zero charge. It is possible that the MC-PDFT results

could be improved by using a larger active space, but studying the active space dependence is beyond the scope of the current work. In the long run, we would like to be able to get good results with a systematic choice of active space, preferably with a minimal size of the active space, and so here we use the systematic nom-CPO scheme, as explained earlier.

4. Summary

This study provides insight into the physical quantities that must be present in a density functional in order to properly predict the dissociation of an ionic bond.

We studied the dissociation of NaCl, which serves as a prototypical system for ionic bonds, and we found that all local Kohn-Sham exchange-correlation density functionals and a majority of Kohn-Sham hybrid exchange-correlation density functionals are unable to correctly dissociate to Na atom and Cl atom, even though some of the functionals yield reasonable dissociation energies at 10 Å due to cancellation of errors. Some of the hybrid functionals with 100% exchange at long range perform well.

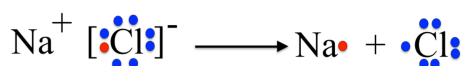
Again considering NaCl, MC-PDFT is able – even with local pair-density functionals – to give very good dissociation energies as compared to KS-DFT, and it also leads correctly to dissociation to neutral atoms for all functionals tested. For MC-PDFT, we emphasize that there is no parameter optimized for the translated functionals, and thus this success can only be attributed to the method itself, that is to the combination of a self-interaction-free multiconfigurational density, pair density, and kinetic energy and a successful on-top pair-density functional.

The AIO molecule presents a different kind of challenge because of high multireference character. The high-level W3X-L method is used to obtain reference energies. All tested hybrid density functional (except B3LYP and PBE0) and pair-density functional calculations give correct neutral dissociation, but the average errors in the bond energy are sometimes larger and sometimes smaller than for NaCl.

Acknowledgments

We are grateful to Laura Gagliardi for many discussions. This work is supported in part by the Air Force Office of Scientific Research by grant no. FA9550-16-1-0134.

TOC Graphic



| | Good De ? | Correct Charge at 10 Å ? |
|---------------|-----------|--------------------------|
| PBE | ✗ | ✗ |
| ftPBE | ✓ | ✓ |
| ω B97X | ✓ | ✗ |
| LC-BLYP | ✓ | ✓ |

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