

Development and Testing new density functionals and their application for molecules

Adrienn Ruzsinszky

Final report

During the two years of postdoctoral work in 2005 and 2007 I have published 12 papers about the title of my project. The work provides an improvement in the areas where existing density functionals exhibit serious failures. I was cooperating with professors John P. Perdew, Gábor I. Csonka, Gustavo Scuseria, Jianmin Tao, and Oleg Vydrov during this work.

I presented my work with the OTKA support in Japan: Remedying Fractional Charge Error of Dissociating Salts by Perdew-Zunger and Scaled Down Self-Interaction Error Correction Adrienn Ruzsinszky, John P. Perdew, Gábor I. Csonka, Oleg Vydrov, Gustavo E. Scuseria XIIth International Congress of Quantum Chemistry, Kyoto, Japan, May 21-26, 2006. Further papers and talks were presented at 10 different conferences financed by myself and NSF during 2005-2007.

In the following summary I focus on the published results, show the most important ideas in the papers through the abstracts.

Abbreviations: local spin density approximation (LSDA), Perdew-Burke-Ernzerhof (PBE), generalized gradient approximation (GGA), Tao-Perdew-Staroverov-Scuseria (TPSS) meta-GGA, self-interaction correction (SIC).

The main results of this work

I. Proper elimination of the self interaction error

The self-interaction error was evident long ago within LSDA, and led Perdew and Zunger (PZ) 1981 to propose a self-interaction correction to LSDA or any other density functional approximation. The PZ self-interaction correction works well for stretched bonds and other open systems, but spoils the equilibrium properties of molecules. We have recently developed a scaled-down self-interaction correction that improves the equilibrium properties but deteriorates the physical properties of open systems. Both the original PZ self-interaction correction and our scaled-down version of it are one-electron self-interaction free, but only the former is nearly many-electron self-interaction-free for atoms (even more so than is Hartree-Fock theory). Many-electron self-interaction freedom is especially important for describing the dissociation of cation dimers or neutral molecules, reaction energies and energy barriers, and band gaps for solids. Spurious self-interaction leads to serious errors in the dissociation limits of many binding-energy curves, to overestimated hyperpolarizabilities of long-chain molecules, to underestimates of bond-length alternation in polymers, to wrong electronic configurations in oxides of d- or f-metals, etc. The problem of properly eliminating the self-interaction error was also solved.

II: van-der-Waals-interaction-corrected functionals

We have made potential energy curve tests for density functionals. The idea behind this is that good equilibrium molecular structure and total energy are not sufficient for many applications (including molecular dynamics), so we have shown how density functionals perform for the whole potential energy curve and its derivatives. We suggested distinguishing between long-range and short-range parts of the weak intermolecular interactions, and we have found GGA's and meta-GGA's that are able to describe the short-range part reasonably well.

III. GGA's for solids

We have recently developed a nonempirical GGA that gives significant improvements for lattice constants, crystal structures, and metal surface energies over existing GGA's. In our new PBEsol, we keep the original PBE form but changed the second-order gradient coefficients for exchange and correlation to satisfy solid-like constraints. Results on lattice constants show an improvement upon the original PBE. Our test set of 18 solids was distributed over simple metals, semiconductors, ionic solids, and transition metals, and showed essentially 0% error in the lattice constant, when compared to experimental values extrapolated to absolute zero temperature and corrected for zero-point anharmonic expansion. The lesson we take from our PBEsol work is that good lattice constants can be achieved when the correct Antoniewicz-Kleinman second-order gradient expansion for exchange is restored *over a wide range of solid-state-like densities*. The TPSS meta-GGA already recovers this expansion, but only for solid-like densities that are very slowly-varying over space. We will construct a new meta-GGA with an expanded range.

Detailed discussion the results with references and citations

The first problem in my research plan was solved in the paper Csonka, G. I.; **Ruzsinszky, A.**; Perdew, J.P. Estimation, Computation and Experimental Correction of Molecular Zero-Point Vibrational Energies *J. Phys. Chem. A* **2005**, *109*, 6779-6789. This paper was accepted just before I started the PD project.

The next problem was to identify the errors of DFT functionals for dissociating molecules, potential curves and small water clusters. We published the following papers about this topic:

Binding Energy Curves from Nonempirical Density Functionals. I. Covalent Bonds in Closed-Shell and Radical Molecules

J. Phys. Chem. A **2005**, *109*, 6779-6789

(Times Cited: 11)

Binding or potential energy curves have been calculated for the ground state diatomics H_2^+ , He_2^+ , LiH^+ , H_2 , N_2 , and C_2 , for the transition state H_3 , and for the triplet first excited state of H_2 , using the nonempirical density functionals from the first three rungs of a ladder of approximations: the LSDA, the PBE, and the TPSS. Good binding energy curves in agreement with coupled-cluster or configuration interaction calculations are found from the PBE GGA, and especially from the TPSS meta-GGA. Expected exceptions are the symmetric radicals H_2^+ , and He_2^+ , where the functionals suffer from self-interaction error, and the exotically bonded C_2 . While the energy barrier for the reaction $H_2 + H \rightarrow H + H_2$ is better in PBE than in TPSS, the transition state H_3 is a more properly positioned and curved saddle-point of the energy surface in TPSS. The triplet first excited state of H_2 obeys the aufbau principle and thus is one of the exceptional excited states that are computable in principle from the ground-state functional. The PBE GGA and TPSS meta-GGA are useful not only for chemical applications, but also for the construction of higher-rung nonempirical functionals that could further improve the binding energy curves.

Binding Energy Curves from Nonempirical Density Functionals II. Van der Waals Bonds in Rare-Gas and Alkaline-Earth Diatomics

J. Phys. Chem. A **2005**, *109*, 6779-6789.

(Times Cited: 19)

Binding energy curves have been calculated for the ground state rare-gas diatomics Ne₂ and Ar₂ and for the alkaline-earth diatomic Be₂ using the nonempirical density functionals from the first three rungs of a ladder of approximations. Binding energy curves in reasonable agreement with those constructed from experiment are found from PBE and TPSS, which incorporate inhomogeneity corrections that satisfy the Lieb-Oxford bound and so describe the short-range part of the van der Waals interaction. At large internuclear separation, these functionals produce an exponentially decaying attraction in place of the correct long-range $-C_6/R^6$. Basis set and exchange-only effects are also discussed.

Proper Gaussian Basis Sets for Density Functional Studies of Water Dimers and Trimers

J. Phys. Chem. B. **2005**, *109*, 21471-21475.

(Times Cited: 12)

The accuracy of PBE and TPSS density functionals for describing non-covalent interaction energies in small water clusters is studied by testing 11 basis sets on a reduced test set proposed by Dahlke and Truhlar [*J. Phys. Chem. B*, 2005, 109, 15677]. We have also tested variants of the PBE functional and the Becke98 hybrid functional. While moderate basis sets give converged density functional theory results for covalent dissociation energies, this is not true for noncovalent interaction energies. Our results show that density functionals give converged interaction energies with aug-cc-pVTZ and aug-cc-pVQZ basis sets. Gradual simplification of the basis set introduces an increasing overbinding effect. The best agreement with the high level result was obtained by the PBE functional at the basis set limit. The converged TPSS interaction energies show a systematic underbinding effect that can be compensated by a somewhat systematic overbinding basis set effect of smaller basis sets such as 6-31+G(d,2p). The inclusion of the diffuse functions in the oxygen basis set is very important, while the inclusion of the f functions practically does not influence the results. Improvement can be obtained by adding more hydrogen p functions to the 6-31+G basis set.

The next main topic was the self-interaction error that spoils the results of the DFT. During this work we introduced a new concept, the **many-electron self-interaction-freedom**.

Scaling down the Perdew-Zunger self-interaction correction in many-electron regions

J. Chem. Phys. **2006**, *124*, 094108.

(Times Cited: 18)

Semilocal density functional approximations (DFAs) for the exchange-correlation energy suffer from self-interaction error, which is believed to be the cause of many of the failures of common DFAs, such as poor description of charge transfer and transition states of chemical reactions. The standard self-interaction correction (SIC) of Perdew and Zunger mends some of these failures but spoils such essential properties as thermochemistry and equilibrium bond lengths. The Perdew-Zunger SIC seems to overcorrect many-electron systems. In this paper, we propose a modified SIC, which is scaled down in many-electron regions. The new SIC has an improved performance for many molecular properties, including total energies, atomization energies, barrier heights of chemical reactions, ionization potentials, electron affinities, and bond lengths. The LSDA benefits from SIC more than higher-level functionals do. The scaled-down SIC has only one adjustable parameter. Rationalization of the optimal value of this parameter enables us to construct an almost-nonempirical version of the scaled-down SIC-LSDA, which is significantly better than uncorrected LSDA and even better than the uncorrected generalized gradient approximation. We present an analysis of the formal properties of the scaled-down SIC and define possible directions for further improvements. In particular, we find that exactness for all one-electron densities does not guarantee correct asymptotics for the exchange-correlation potential of a many-electron system.

Spurious fractional charge on dissociated atoms: Pervasive and resilient self-interaction error of common density functionals

J. Chem. Phys. **2006**, *125*, 194112

(Times Cited: 17)

Semi-local density functional approximations for the exchange-correlation energy can improperly dissociate a neutral molecule XY ($Y \neq X$) to fractionally charged fragments $X^{+q} \cdots Y^{-q}$ with energy significantly lower than $X^0 \cdots Y^0$. For example NaCl can dissociate to $Na^{+0.4} \cdots Cl^{-0.4}$. Generally, q is positive when the lowest unoccupied orbital energy of atom Y^0 lies below the highest occupied orbital energy of atom X^0 . The first 24 open sp -shell atoms of the periodic table can form 276 distinct unlike pairs XY , and in the local spin density approximation 174 of these display fractional-charge dissociation. Finding these lowest-energy solutions with standard quantum chemistry codes can however require special care. SIC semi-local approximations are exact for one-electron systems, and also reduce the spurious fractional charge q . The original SIC of Perdew and Zunger typically reduces q to 0. A scaled-down SIC with better equilibrium properties sometimes fails to reduce q all the way to 0. The desideratum of “**many-electron self-interaction-freedom**” is introduced as a generalization of the one-electron concept.

Density functionals that are one- and two- are not always many-electron self-interaction free, as shown for H_2^+ , He_2^+ , LiH^+ , and Ne_2

J. Chem. Phys. **2007**, *126*, 104102

(Times Cited: 17)

The common density functionals for the exchange-correlation energy make serious self-interaction errors in the molecular dissociation limit when real or spurious non-integer electron numbers N are found on the dissociation products. An “ M -electron self-interaction-free” functional for positive integer M is one that produces a realistic linear variation of total energy with N in the range $M - 1 < N \leq M$, and so can avoid these errors. This desideratum is a natural generalization to all M of the more familiar one of one-electron self-interaction freedom. The intent of this paper is not to advocate for any functional, but to understand what is required for a functional to be M -electron self-interaction-free and thus correct even for highly-stretched bonds. The original Perdew-Zunger SIC and our scaled-down variant of it are exactly one- and nearly two-electron self-interaction free, but only the former is nearly so for atoms with $M > 2$. Thus all these SIC’s produce an exact binding energy curve for H_2^+ , and an accurate one for He_2^+ , but only the unscaled Perdew-Zunger produces an accurate one for Ne_2^+ , where there are more than 2 electrons on each fragment $Ne^{+0.5}$. We also discuss LiH^+ , which is relatively free from self-interaction errors. We suggest that the ability of the original and unscaled Perdew-Zunger SIC to be nearly M -electron self-interaction-free for atoms of all M stems in part from its formal resemblance to Hartree-Fock theory, with which it shares a sum rule on the exchange-correlation hole of an open system.

Exchange and Correlation in Open Systems of Fluctuating Electron Number

Phys. Rev. A **2007**, *76*, 040501(R)

(Times Cited: 9)

Semi-local density functionals for the exchange-correlation energy fail for separated open systems of fluctuating electron number (as in stretched molecules A_2^+ , or solid transition metal oxides). For an open system with fractional occupation numbers, we develop an exact-exchange theory and an exchange-hole sum rule that explain the errors and suggest a way to correct them via a local hybrid functional. While the exact correlated energy varies linearly

with average electron number between adjacent integers, the semi-local energy is curved upward and the exchange-only or Hartree-Fock downward.

Diminished gradient dependence of density functionals: Constraint satisfaction and self-interaction correction

J. Chem. Phys. **126**, 244107 (2007).

(Times Cited: 3)

The PBE GGA for the exchange-correlation energy functional has two nonempirical constructions, based on satisfaction of universal exact constraints on the hole density or on the energy. We show here that, by identifying one possible free parameter in exchange and a second in correlation, we can continue to satisfy these constraints while diminishing the gradient dependence almost to zero (i.e., almost recovering the LSDA). This points out the important role played by the Perdew-Wang 1991 nonempirical hole construction in shaping PBE and later constructions. Only the undiminished PBE is good for atoms and molecules, for reasons we present, but a somewhat diminished PBE could be useful for solids; in particular, the surface energies of solids could be improved. Even for atoms and molecules, a strongly diminished PBE works well when combined with a scaled-down self-interaction correction (although perhaps not significantly better than LSDA). This shows that the undiminished gradient dependence of PBE and related functionals works somewhat like a scaled-down self-interaction correction to LSDA.

Understanding and correcting the self-interaction error in the electrical response of hydrogen chains

Phys. Rev. A **2008**, 77, 060502(R).

(Times Cited: 2)

Semilocal density functionals such as the local-spin-density and generalized-gradient approximations are known to overestimate the polarizabilities and especially the hyperpolarizabilities of long-chain molecules, the latter by as much as a factor of 10 or more in model hydrogen chains. These quantities are much better predicted by exact-exchange methods such as Hartree-Fock or optimized effective potential. We show here that the semilocal functionals, after full or scaled-down Perdew-Zunger SIC, are about as good as the exact-exchange methods for these quantities. As is the case for the exact-exchange methods, SIC is fully nonlocal and exact for all one-electron densities, and tends to maintain an integer number of electrons on each H₂ chain unit to a greater extent than the semilocal functionals do. In this study, the SIC energy is minimized directly, without an optimized effective potential.

Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces.

Phys. Rev. Lett. **2008**, 100, 136406.

(Times Cited: 15)

Popular modern generalized gradient approximations are biased toward the description of free-atom energies. Restoration of the first-principles gradient expansion for exchange over a wide range of density gradients eliminates this bias. We introduce a revised PBE GGA that improves equilibrium properties of densely packed solids and their surfaces.