Department of Energy, Basic Energy Sciences, Chemical Theory and Computation
Principal Investigator (PI): **Adrienn Ruzsinszky**
PI's Institution: **Temple University**
Street Address/City/State/Zip: **1925 N.12th Street, Philadelphia, PA 19122**
PI Postal Address: **Department of Physics**
PI Email: **aruzsinszky@temple.edu**

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Previous Project title: Exploring the Random Phase Approximation for Materials and Chemical Physics

Postdocs: Savio Laricchia**,** Jefferson Bates
Graduate student: Niladri Sengupta

Scope of the work

In this work we test the performance of the fully nonlocal random phase approximation (RPA) for challenging problems in materials chemistry and physics.

The Random Phase Approximation (RPA) is becoming a standard method beyond semi-local Density Functional Theory that naturally incorporates weak interactions and eliminates self-interaction error in the exchange energy. RPA is not perfect, however, and suffers from self- correlation error as well as an incorrect description of short-ranged correlation. To improve upon RPA, a beyond-RPA correction must be included in the calculation of the correlation energy. In this work we have explored various beyond-RPA corrections such as nonempirical kernels based on exact constraints and the second-order screened exchange (SOSEX).

In this project we reveal the strengths and limitations of the RPA and its corrections through some materials problems focusing on structural phase transitions, weak interactions, water clusters and transition metal chemistry.

Structural phase transitions require high accuracy. We have assessed the performance of the non-self-consistent random phase approximation (RPA) on two pressure-induced structural phase transitions, diamond to β-Sn Si in Si and α-quartz to stishovite in SiO2. The calculated equilibrium lattice properties of the four structures are in better agreement with experimental results than are those from several semilocal functionals. We found that the RPA error cancellation is nearly perfect in many solids, including Si, but less perfect in solid SiO_2, as it is in many chemical reactions.

Along with other density functional approximations, we have assessed the RPA for the ground-state magnetism and electronic structure of a strongly correlated metal, rutile VO2. Using recent quantum Monte Carlo results as the benchmark, all tested semilocal and hybrid functionals as well as the RPA (with PBE inputs) predict the correct magnetic ground states for rutile VO2.

Despite the nonlocal nature of its exchange and correlation, the so-called direct RPA (dRPA) has several flaws due to its selfcorrelation error. In order to obtain accurate and precise reaction energies, barriers and noncovalent intra- and intermolecular interactions, we construct a new dual-hybrid dRPA (dRPA75: hybridization of exact and semilocal exchange in both the energy and the orbitals) and test the performance of this new functional on isogyric, isodesmic, hypohomodesmotic, homodesmotic, and hyperhomodesmotic reaction classes. We also used a test set of 14 Diels−Alder reactions, six atomization

energies (AE6), 38 hydrocarbon atomization energies, and 100 reaction barrier heights (DBH24, HT-BH38, and NHT-BH38). For noncovalent complexes, we used the NCCE31 and S22 test sets. To test the intramolecular interactions, we used a set of alkane, cysteine, phenylalanine-glycine-glycine tripeptide, and monosaccharide conformers.. We show that a universally accurate description of chemical properties can be provided by a large, 75% exact exchange mixing both in the calculation of the reference orbitals and the final energy.

RPA has been shown to yield superior results to semilocal functionals for main group thermochemistry, but much less is known about its performance for transition metals. We have therefore analyzed the behavior of reaction energies, barrier heights, and ligand dissociation energies obtained with RPA and compare our results to several semilocal and hybrid functionals. Particular attention was paid to the reference determinant dependence of RPA. We found that typically the results do not vary much between semilocal or hybrid functionals as a reference, as long as the fraction of exact exchange (EXX) mixing in the hybrid functional is small. For large reactions of EXX mixing, however, the Hartree−Fock-like nature of the determinant can severely degrade the performance. Overall, RPA systematically reduces the errors of semilocal functionals and delivers excellent performance from a single reference determinant for inherently multireference reactions. The behavior of dual hybrids that combine RPA correlation with a hybrid exchange energy was also explored, but ultimately did not lead to a systematic improvement compared to traditional RPA for these systems.

The performance of RPA and beyond-RPA approximations for the treatment of electron correlation was benchmarked on three different molecular test sets. The test sets were chosen to represent three typical sources of error which can contribute to the failure of most density functional approximations in chemical reactions. The first test set (atomization and n-homodesmotic reactions) offers a gradually increasing balance of error from the chemical environment. The second test set (Diels-Alder reaction cycloaddition = DARC) reflects more the effect of weak dispersion interactions in chemical reactions. Finally, the third test set (self-interaction error 11 = SIE11) represents reactions which are exposed to noticeable self-interaction errors.
In all our tests, we prefered to apply RPA with PBE orbitals as a reference (RPA@PBE). The choice is very well justified especially for the DARC reactions test. RPA@PBE provides far the best accuracy for this data set. The conclusion from the results is relevant. The inclusion of the Hartree-Fock exchange in the reference of RPA deteriorates the results, confirming that dispersion interactions govern the reactions of the DARC set. Finally, the SIE11 test set confirms that the self-interaction or delocalization error clearly needs the “beyond-RPA” treatment, as confirmed by the best performance of the rPT2 approximation. Our result show that overall the second-order renormalized RPA method (rPT2) approximation gives good accuracy in most tests. In certain tests, the rPT2 method’s wider applicability can be somewhat limited by the SOSEX approach. The results also provide some hint for the need of an intrinsic kernel correction to the RPA.

The major computational bottleneck of RPA is its strong dependence on the basis set utilized. We studied the basis set convergence of the dRPA correlation energies on a set of 65 hydrocarbon isomers from CH4 to C6H6. We calculated the iterative density fitted dRPA correlation energies using an efficient algorithm based on the CC-like form of the equations using the self-consistent Hartree-Fock orbitals. We tested the popular inverse cubic, the optimized exponential, and inverse power formulas for complete basis set extrapolation. We have found that the optimized inverse power based extrapolation delivers the best energies. Further analysis showed that the optimal exponent depends on the molecular structure, and the most efficient two-point energy extrapolations that use X = 3 and 4 can be improved considerably by considering the atomic composition and hybridization states of the atoms in the molecules. Our results also show that the optimized exponents that yield accurate X = 3 and 4 extrapolated dRPA energies for atoms or small molecules might be inaccurate for larger molecules.

The correct description of the interaction between anions and aromatic rings might be used for the design of selective anion receptors and channels, and this is important for advances in the field of supramolecular chemistry. In this paper we focus on the so-called anion−π interaction. For 30 π−anion−π′ sandwich complexes we have calculated RPA binding energies for benchmarks. Among the investigated methods, the RPA/ATZ (ATZ: Dunning's correlation consistent triple-zeta basis set) model chemistry is quite accurate, precise, and efficient so we suggest using it for solving chemical and biological problems of moderate size.

In water clusters, there is a delicate balance of van der Waals interactions and hydrogen bonds. Although semilocal and nonlocal density functional approximations have been recently routinely applied to water in various phases, the accurate description of hydrogen bonds remains a challenge. The most popular density functional approaches fail to predict the correct ordering of the energies of water clusters. Our recently constructed dual-hybrid dRPA75 approximation is a successful combination of exact and semilocal exchange, and nonlocal correlation in its energy, while utilizing a high fraction of exact exchange. We have shown that the dRPA75 method has a systematic error, which can be efficiently compensated for by the aug-cc-pVTZ basis set for small- and medium-sized water clusters.

In order to remedy some of the shortcomings of RPA within adiabatic connection fluctuation-dissipation (ACFD) density functional theory, we introduced a short-ranged, exchange-like kernel that is one-electron self-correlation free and exact for two-electron systems in the high-density limit. By tuning a free parameter in our model to recover an exact limit of the homogeneous electron gas correlation energy, we obtain a nonlocal, energy-optimized kernel that reduces the errors of RPA for both homogeneous and inhomogeneous solids. We also demonstrated the kernel's capability to describe the dominant correlation effects with a low-order expansion in both metallic and nonmetallic systems.
Satisfying exact constraints, this model kernel can be a more general substitute for other expensive beyond-RPA corrections for materials.

Publications acknowledging this Grant in 2013-2016

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