

Exchange-correlation functionals for chemical accuracy and van der Waals interactions: Implementation of the adiabatic-connection fluctuation-dissipation theorem and application to H₂ and Be₂

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In studies of molecules and solids using density-functional theory, one often achieves a useful accuracy within the traditional local-density or generalized-gradient approximations for exchange-correlation. Yet both fall short of giving total energies with chemical accuracy and do poorly for van der Waals systems. Systematic progress in both respects is expected from the (in principle exact) representation of the exchange-correlation functional through the adiabatic-connection fluctuation-dissipation theorem (ACFDT). There the electronic pair-correlations are obtained by a coupling-strength integration of the dynamical density response.

In this talk I will present our implementation of the ACFDT formalism within a pseudopotential plane-wave method [1]. Taking the He atom as an example, I will illustrate the accuracy of this approach and examine practical approximations such as the random phase approximation (RPA) in conjunction with a local-density correction for short-range correlations [2]. I will then discuss our results for the binding energy of the H₂ and Be₂ dimers where we find that chemical accuracy is indeed achieved within the RPA [3]. Finally I will describe further tests with the RPA, considering stretched configurations of Be₂ and the van der Waals limit.

Our results clearly demonstrate that ACFDT XC functionals are now computationally feasible and are a promising candidate for the accurate description of atomic potential energy surfaces all the way from the bonding to the van der Waals regime.

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- [1] Part of the ABINIT package <http://www.mapr.ucl.ac.be/Fr/PCPM/ABINIT/>.
 - [2] Z. Yan, J.P. Perdew, and S. Kurth, Phys. Rev. B 61, 16430 (2000).
 - [3] M. Fuchs and X. Gonze, in preparation.