

# Using parameters from a density functional theory model to add dispersion corrections to model noncovalent interactions



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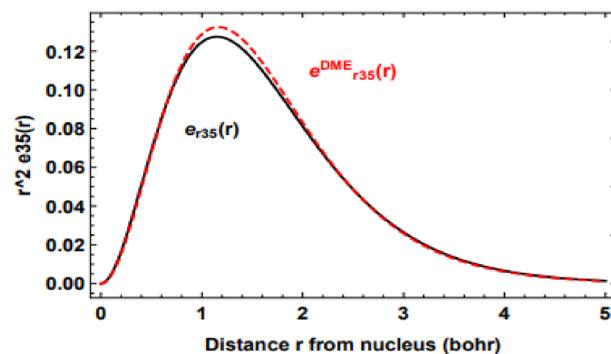
## Density Functional Theory Introduction

Density Functional Theory (DFT) calculations are widely used and important for validating proposed reaction mechanisms, validating chemical structures, and predicting how chemical functionalization changes properties of a compound for example reaction rates, absorbance, and fluorescence spectra describing the need for new inexpensive DFT functionals.

DFT combines a "freshman chemistry" molecular orbital calculation with a correction for the correlation between different electrons' positions and momenta. Even though an exact correction exists, an approximated value must be used in practice as a function of various ingredients.

## Density Matrix Expansion (DME)

A baseline for what the overlap of occupied molecular orbitals onto an *s* like orbital test function centered at point *r* would be for a normal slowly varying electron gas system is needed. This baseline is derived by substituting the DME expression of a slowly varying electron gas into the rung 3.5 test function. DME provides a foundation for practical, minimally empirical, nonlocal correlation functionals compatible with full nonlocal local exchange. Adding the DME parameter gives an accurate representation of the true exchange energies.



The above black graph shows the actual ground state of a hydrogen atom using the normal rung 3.5 ingredient. The red graph shows the DME parameter implemented as a good approximation for the ground state of a hydrogen atom.

DFA	Basic+small	Iso+large	Barrier
HFPBE	11.1	17.0	21.5
PBE	6.8	16.2	15.4
SCAN	5.6	9.0	14.5
B3LYP-D3	4.2	10.3	9.0
M06-2X	2.7	6.1	5.0

The above table compares weighted mean absolute deviation (kcal/mol) for commonly used approximate DFAs.

Iso+large: Reaction energies for large systems and isomerization reactions

Basic+small: Reaction energies for small systems and basic reactions

## Abstract

Dispersion interactions also known as van der Waals interactions are essential for everything from nanomaterials to organic chemistry to biological chemistry. Modeling that chemistry requires modeling van der Waals interactions. Approximations that start from "freshman chemistry" molecular orbital (MO) theory do not account for dispersion. For example, helium-helium interactions are unbound in molecular orbital theory as two electrons are placed in antibonding orbital, but in reality, the interactions are weakly bound and can form a liquid. We have developed a density functional theory method embodying MO theory and corrections. Dispersion corrections can be added to noncovalent interactions in order to model them by using a standard model with different parameters. By fitting these parameters, the accurate known bond energies of real noncovalent complexes can be reproduced.

## Incorporating DME with Dispersion Corrections

Density Matrix Expansion can be incorporated with dispersion corrections to give the best representation with lowest error. Dispersion corrections are added to noncovalent interactions in order to model them by using a standard model with different parameters. By fitting these parameters, the accurate known bond energies of real noncovalent complexes can be reproduced.

## Error Results

**HFPBE method:** Density functional approximation (DFA) method without density matrix expansion correction

**HFPBE-D3(BJ) method:** Density functional approximation containing rung 3.5 density matrix expansion correction

Adding the dispersion correction lowers the mean absolute error energy from 1.27 kcal/mol to 0.75 kcal/mol. Adenine thymine stack shows the lowest mean absolute error without a dispersion correction. Formic acid dimer shows the lowest mean absolute error with the dispersion correction present.

Method	Mean absolute Error (kcal/mol)	Molecule
No dispersion correction (HFPBE)	1.27	Adenine Thymine Stack
Dispersion correction present (HFPBE-D3(BJ))	0.75	Formic Acid Dimer

A specific set of added parameters (*s8*, *a1*, and *a2*) gives the resulting dispersion correction with the lowest error (0.75). This parameter set is found to be  $iop(3/175=0700000,3/177=0300000,3/178=5800000)$ .



Adenine Thymine Stack

## Formic Acid Example

### Formic Acid Dimer Example:

Five formic acid dimer representations are evaluated. Each dimer has a different equilibrium bond distance. The bond distances include 90%, 100%, 120%, 150%, and 200% of the known equilibrium bond. In addition, each monomer is evaluated for nuclear repulsion energy, nuclear repulsion energy with the dispersion correction, and how much the dispersion correction contributes to the binding energy.

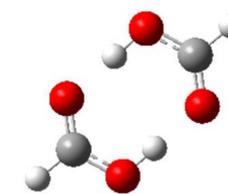
Molecule	Nuclear Repulsion Energy (kJ/mol)	Nuclear Repulsion Energy w/ Correction (kJ/mol)	Dispersion Correction Energy (kJ/mol)	Dispersion Contribution to Binding Energy (kJ/mol)
Dimer with 90% dist.	632927.59	632919.24	-8.35	-3.92
Dimer with 100% dist.	619477.85	619469.75	-8.10	-3.67
Dimer with 120% dist.	596353.61	596346.06	-7.55	-3.12
Dimer with 150% dist.	568662.92	568656.21	-6.71	-2.28
Dimer with 200% dist.	534789.81	534784.22	-5.59	-1.15
1 <sup>st</sup> Monomer	184088.99	184086.77	-2.22	
2 <sup>nd</sup> Monomer	184088.99	184086.77	-2.22	

Dispersion correction is found by subtracting the nuclear repulsion energy from the nuclear repulsion energy with the dispersion correction.

Dispersion correction contribution to the binding energy is found by subtracting the dispersion correction energy of each monomer from the dispersion correction of the dimer.

As shown in the data, as the distance between the dimers increases, the dispersion correction energy and the dispersion correction contribution to the binding energy both decrease.

## Molecules



Formic Acid Dimer – 90% distance



Formic Acid Dimer – 200% distance

## Acknowledgements

Calculations were supported by TCU high performance computing center.