Dispersion Interactions from the Exchange-Hole Dipole Moment.

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$$E_{\text{disp}} = -\frac{1}{2} \sum_{ij} \frac{C_6 f_6(R_{ij})}{R_{ij}^6} + \left[ \frac{C_8 f_8(R_{ij})}{R_{ij}^8} + \frac{C_{10} f_6(R_{ij})}{R_{ij}^{10}} + \ldots \right]$$

comes from perturbation theory:

$$E^{(2)} = \frac{\langle \hat{V}_{\text{int}}^2 \rangle}{\Delta E}$$

where:

- Interaction between neutral fragments (classical electrostatic interactions already captured at semilocal level).
- Asymptotic expression.

The exchange-hole model

\[
h_{x\sigma}(1, 2) = -\frac{|\rho_{1\sigma}(1, 2)|^2}{\rho_{1\sigma}(1)}
\]

- Probability of exclusion of same-spin electron.
- On-top depth condition: \( h_{x\sigma}(1, 1) = -\rho_{1\sigma}(1) \)
- Normalization: \( \int h_{x\sigma}(1, 2) d2 = -1 \) for all \( 1 \).
- \( \rho_{1\sigma}(1, 2) = \sum_i \psi_i^*(1)\psi_i(2) \)
The exchange-hole model

- **Model for dispersion:** interaction of electron-hole dipoles.
- **Dipole:** $d_{x\sigma}(r) = \int r' h_{x\sigma}(r, r') dr' - r$
- **Assumption:** dipole oriented to nearest nucleus.

$$\langle M^2_i \rangle_i = \sum_\sigma \int \omega_i(r) \rho_\sigma(r) [r_i^l - (r_i - d_{X\sigma})]^2 dr.$$  

The Becke-Roussel model of exchange-hole

- **Becke-Roussel model** of $h_x$.
  (PRA 39 (1989) 3761)

**Parameters (A,a,b) obtained:**
- Normalization
- Value at reference point.
- Curvature at reference point
  *(reqs. kinetic energy density).*

**Advantages:**
1. Semilocal model of the dipole ($d_x = b$).
2. XDM dispersion model $\rightarrow$ meta-GGA.

The XDM equations: interaction coefficients

Multipole moments

\[ \langle M^2 \rangle_i = \sum_\sigma \int \omega_i(r) \rho_\sigma(r) \left[ r^l_i - (r_i - d_{X\sigma})^l \right]^2 dr \]

use Hirshfeld atomic partition:

\[ \omega_i(r) = \frac{\rho_{i\text{at}}(r)}{\sum_j \rho_{j\text{at}}(r)} \]

Non-empirical dispersion coefficients. \textit{n-body and any order}. For instance:

\[ C_{6,ij} = \frac{\alpha_i \alpha_j \langle M^2 \rangle_i \langle M^2 \rangle_j}{\langle M^2 \rangle_i \alpha_j + \langle M^2 \rangle_j \alpha_i} \]

We include: two-body terms \( C_6, C_8 \) and \( C_{10} \).

Implementation for molecules

XDM implemented post-\textbf{Gaussian 09} using the \texttt{postg} program. Also \texttt{nwchem} (available upon request).

From the wfn file, \texttt{postg} gives:

- XDM dispersion coefficients, volumes, polarizabilities
- XDM dispersion energy
- forces for geometry optimization (fixed coefficients)
- second derivatives for frequencies
- Hirshfeld charges

Download \texttt{postg} from the XDM page at:

\url{http://faculty1.ucmerced.edu/ejohnson29}


Implementation for solids

- **PS/PW (Quantum ESPRESSO)**

- Solids – Uniform 3D grid:
  - $d_{x\sigma}$, valence $\tau$, $\rho$.
  - $\omega_i$, all-electron $\rho$, $\rho_{at}$.

- Computational cost.
  - Comparable to DFT-D.
  - $E_{\text{disp}}$ fast compared to $E_{\text{DFT}}$.

- Optimization: atomic forces and stresses.

<table>
<thead>
<tr>
<th>$n_{\text{grid}}$</th>
<th>64</th>
<th>80</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6$ (C-C)</td>
<td>22.300</td>
<td>22.425</td>
<td>22.426</td>
</tr>
<tr>
<td>$C_6$ (O-O)</td>
<td>11.580</td>
<td>11.627</td>
<td>11.627</td>
</tr>
<tr>
<td>$E_{\text{disp}}$ (Ry)</td>
<td>-0.062965</td>
<td>-0.063374</td>
<td>-0.063374</td>
</tr>
</tbody>
</table>

Damping function parametrization

\[ E_{\text{disp}} = \frac{1}{2} \sum_{ij} \frac{C_6f_6(R_{ij})}{R_{ij}^6} + \left[ \frac{C_8f_8(R_{ij})}{R_{ij}^8} + \frac{C_{10}f_6(R_{ij})}{R_{ij}^{10}} + \ldots \right] \]

\[ f_n(R_{ij}) = \frac{R_{ij}^n}{R_{ij}^n + (a_1 R_{ij,c} + a_2)^n} \]

Kannemann-Becke 65-set.

Supercell calculations.
Parametrization set

49 gas-phase dimers from Kannemann and Becke; JCTC 6 (2010) 1081.

- noble gases
- dispersion
- $\pi$-stacking
- dipole - induced dipole
- mixed
- dipole - dipole
- hydrogen-bonding
Statistics of the fit (solids)

**Statistics for supercell (PS/PW) and Gaussian calculations.**

<table>
<thead>
<tr>
<th>Training set (KB49)</th>
<th>B86bPBE</th>
<th>PW86PBE</th>
<th>BLYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_1)</td>
<td>0.684</td>
<td>0.407</td>
<td>0.934</td>
</tr>
<tr>
<td>(a_2(\text{Å}))</td>
<td>1.368</td>
<td>2.415</td>
<td>0.965</td>
</tr>
<tr>
<td>MAE (kcal/mol)</td>
<td>0.41</td>
<td>0.46</td>
<td>0.42</td>
</tr>
<tr>
<td>MAPE</td>
<td>11.3</td>
<td>13.8</td>
<td>11.8</td>
</tr>
</tbody>
</table>

**S22**

| MAE (kcal/mol)      | 0.43    | 0.46    | 0.35  | 0.32  | 0.22  |
| MAPE                | 7.00    | 8.12    | 5.92  | 8.24  | 4.85  |
Statistics of the fit (molecules)

XDM with aug-cc-pVTZ; mean absolute errors in kcal/mol.

Pure functionals:

<table>
<thead>
<tr>
<th>Quantity</th>
<th>BLYP</th>
<th>PW86</th>
<th>PBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAE</td>
<td>0.31</td>
<td>0.40</td>
<td>0.50</td>
</tr>
<tr>
<td>MA%E</td>
<td>9.8</td>
<td>11.8</td>
<td>14.3</td>
</tr>
</tbody>
</table>

Hybrid and range-separated functionals:

<table>
<thead>
<tr>
<th>Quantity</th>
<th>B3LYP</th>
<th>BH&amp;HLYP</th>
<th>PBE0</th>
<th>CAM-B3LYP</th>
<th>LC-ωPBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAE</td>
<td>0.28</td>
<td>0.37</td>
<td>0.41</td>
<td>0.39</td>
<td>0.28</td>
</tr>
<tr>
<td>MA%E</td>
<td>6.7</td>
<td>7.8</td>
<td>10.2</td>
<td>8.3</td>
<td>7.8</td>
</tr>
</tbody>
</table>
Role of exchange

The exact exchange potential decays as $-1/r$ far from a molecule.

In terms of the exchange hole, $h_X$ remains on the molecule as the reference point moves away from it.

The $-1/r$ asymptotic dependence was used to design the B88 exchange functional.

Functionals based on B88 or range-separated hybrids with the full exact-exchange limit (LC-$\omega$PBE) give more accurate intermolecular exchange contributions.
### Benchmark sets

Mean absolute errors in XDM binding energies with aug-cc-pVTZ

<table>
<thead>
<tr>
<th></th>
<th>LYP</th>
<th>PW86</th>
<th>B3LYP</th>
<th>LC-ωPBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>S22</td>
<td>0.22</td>
<td>0.35</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td>S66</td>
<td>0.22</td>
<td>0.29</td>
<td>0.25</td>
<td>0.20</td>
</tr>
<tr>
<td>HSG</td>
<td>0.20</td>
<td>0.17</td>
<td>0.12</td>
<td>0.23</td>
</tr>
</tbody>
</table>


See JCP **138** (2013) 204109 for additional data.
Graphite

Prediction of sublimation enthalpies

Benchmark:

- No reference wave-function data.
- Experimental **sublimation enthalpies** not directly comparable.

Phase Transition Enthalpy Measurements of Organic and Organometallic Compounds. Sublimation, Vaporization and Fusion Enthalpies From 1880 to 2010

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- 21 crystals, small systems, low polymorphism.
- Well known sublimation enthalpies at or below room temperature.
- Different intermolecular interactions.
\[ \Delta H_{\text{sub}}(V, T) = E_{\text{el}}^{\text{mol}} + E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}}^{\text{mol}} + pV \\
- \left( E_{\text{el}}^{\text{crys}} + E_{\text{vib}}^{\text{crys}} \right) \]

- \( E_{\text{el}}^{\text{crys}} \longrightarrow \text{DFT+dispersion} \)
- \( E_{\text{el}}^{\text{mol}} \longrightarrow \text{DFT+dispersion, supercell} \)
- \( E_{\text{trans}} + E_{\text{rot}} + pV \longrightarrow 4RT (7/2RT) \)
- Rigid molecule approximation \( E_{\text{vib}}^{\text{mol}} = E_{\text{vib}}^{\text{crys}} \) for intramolecular
- Intermolecular \( E_{\text{vib}}^{\text{crys}} \longrightarrow \text{Dulong-Petit 6RT (5RT)} \)
- Zero-point vibrational contributions neglected
- Approximations tested for CO\(_2\) crystal. Average experimental accuracy \( \approx 1 \text{ kcal/mol} \).
# Sublimation enthalpies

<table>
<thead>
<tr>
<th></th>
<th>XDM</th>
<th>DFT-D2</th>
<th>TS09</th>
<th>vdw-DF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(kJ/mol)</td>
<td>B86b</td>
<td>PW86</td>
<td>PBE</td>
</tr>
<tr>
<td><strong>MAE</strong></td>
<td></td>
<td>4.81</td>
<td>6.50</td>
<td>5.35</td>
</tr>
<tr>
<td><strong>MAPE</strong></td>
<td></td>
<td>6.23</td>
<td>8.00</td>
<td>6.74</td>
</tr>
</tbody>
</table>

Relative error (%)

Prediction of crystal structures

- Vibrational Helmholtz free energy:

\[
F_{\text{vib}}(V, T) = \sum_{j=1}^{3n} \left[ \frac{\omega_j}{2} + k_B T \ln \left( 1 - e^{-\omega_j/k_B T} \right) \right]
\]

- Thermal pressure:

\[
p_{\text{th}} = -\frac{\partial F_{\text{vib}}}{\partial V}
\]

- Equilibrium condition:

\[
\frac{\partial E}{\partial V} = p_{\text{th}} = -p_{\text{sta}}
\]

Relax the crystal under negative pressure \(p_{\text{th}}\)
### Crystal structures

![Graph showing relative error in crystal structures](image)

<table>
<thead>
<tr>
<th>Method</th>
<th>XDM</th>
<th>DFT-D2</th>
<th>TS</th>
<th>vdw-DF</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a.u.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B86b</td>
<td>0.12</td>
<td>0.06</td>
<td>0.20</td>
<td>0.11</td>
</tr>
<tr>
<td>PW86</td>
<td>0.20</td>
<td>0.11</td>
<td>0.10</td>
<td>0.31</td>
</tr>
<tr>
<td>PBE</td>
<td>1.31</td>
<td>1.58</td>
<td>4.40</td>
<td>1.88</td>
</tr>
</tbody>
</table>


A. Otero & E. Johnson (UC Merced)
Enantiomeric excess of amino-acids
Enantiomeric excess of amino-acids

A simple model

- Same solvation energies.
- Same crystal temperature effects.
- \( \Delta E = E_{dl} - E_l \)
- Predicted ee:

\[
ee = \frac{\beta^2 - 1}{\beta^2 + 1} \times 100
\]

\[
\beta = e^{-\Delta E/RT}
\]

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>DFT</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Serine</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Histidine</td>
<td>93.5</td>
<td>93.7</td>
</tr>
<tr>
<td>Leucine</td>
<td>92.2</td>
<td>87.9</td>
</tr>
<tr>
<td>Alanine</td>
<td>67.1</td>
<td>60.4</td>
</tr>
<tr>
<td>Cysteine</td>
<td>69.2</td>
<td>58.4</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>70.6</td>
<td>51.7</td>
</tr>
<tr>
<td>Valine</td>
<td>62.3</td>
<td>44.1</td>
</tr>
<tr>
<td>Proline</td>
<td>0.0</td>
<td>39.7</td>
</tr>
<tr>
<td>Aspartic acid</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Enantiomeric excess

Enantiomeric Excess

\( \Delta E \) (kcal/mol)
An electride is an ionic substance in which a localized electron acts as an anion.

Existing electrides require a cage like structure to stabilise the cation: crown ethers and cryptands.

High magnetic susceptibilities, variable conductivities, very strong reducing agents.
Electrides

Use the NCI index to visualize the electrons - JACS 132 (2010) 6498.

Plots regions with low electron density and reduced density gradient.
Electrides

Graphite step edges

Graphite step edges
Summary

1. XDM implemented for gas-phase and solid-state.
2. Excellent benchmarking results.
3. Very accurate lattice energies and crystal geometries.
4. Accurate enough to predict ee in solution.
5. More: electrides, tribology,...

Download postg, QE+XDM, and CRITIC2 from:

http://faculty1.ucmerced.edu/ejohnson29