# The Exchange-Correlation Dipole Moment (XCDM) Model and Z-damping

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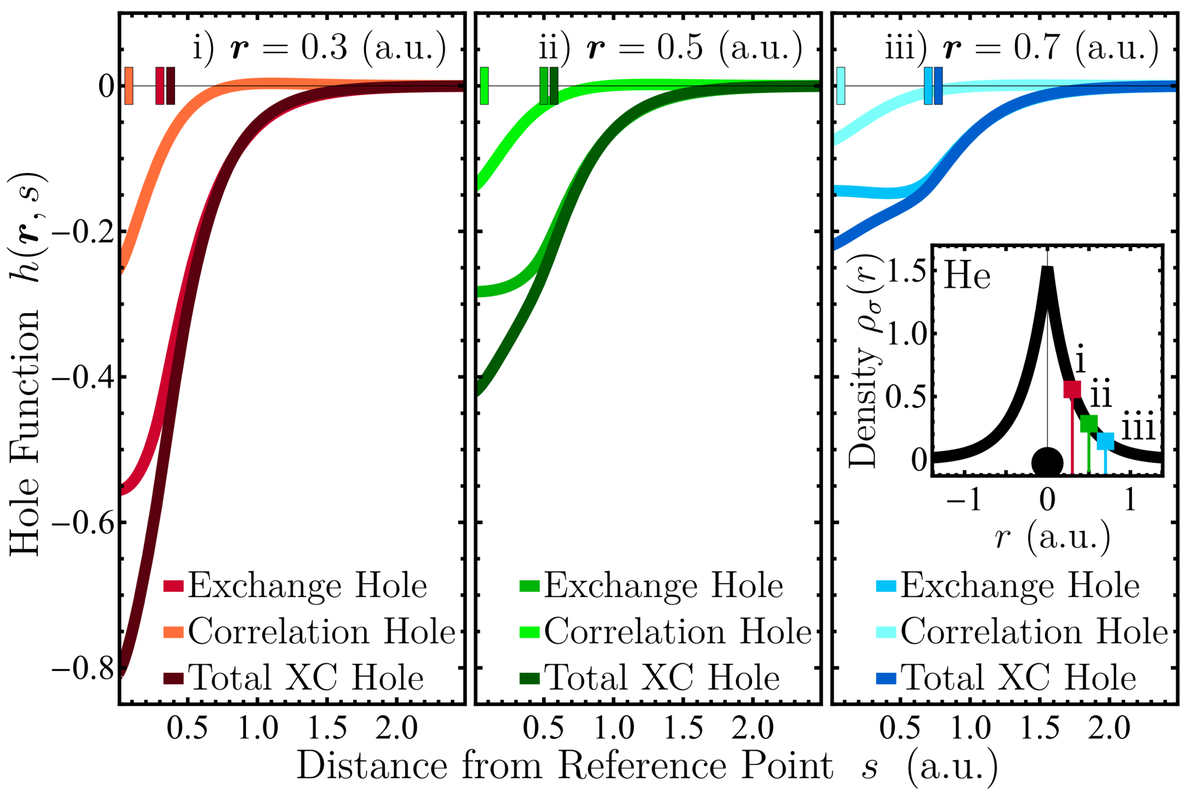
## Introduction and Motivation

Density-functional theory (DFT) has become the workhorse of modern computational chemistry, with dispersion corrections (DCs) such as the exchange-hole dipole moment (XDM) model playing a key role in high-accuracy modelling of large-scale systems [1]. Here, we introduce physics-guided XDM variants: XCDM, which supplements XDM with same- and opposite-spin dynamical correlation [2, 3], and XDM(Z), which implements the novel one-parameter damping function proposed by Becke to address shortcomings BJ-damping showed on alkali-metal clusters [4]. XCDM and Z-damping are now implemented in both Gaussian (via postg) and FHI-aims. XDM and its variants are benchmarked on the comprehensive GMTKN55 database [5] using GGA, global hybrid, and range-separated hybrid functionals, and compared directly to the D3(BJ), TS, MBD@rsSCS, and MBD-NL dispersion corrections. This marks the first time that the XDM and MBD corrections have been tested on GMTKN55. Four solid-state benchmarks testing molecular crystals are also considered.

## Correlation Contribution to the Total XC Hole

For the He atom, three different radial points are chosen for comparison as we plot the exchange hole, opposite-spin correlation hole, and the total exchange-correlation (XC) hole as a function of reference point $s$. Their associated dipole moment strengths are indicated with coloured bars along the $s$-axis. While the exchange hole is a reasonable approximation to the total XC hole, we see that the short-range dynamical correlation contribution is non-negligible and deepens it.




## XCDM & Z-damping Implementation

The XDM and XCDM models calculate the dispersion energy via a pairwise sum

$$E_{\text{disp}} = -\sum_{i<j}\sum_{n=6,8,10} \frac{f_n(R_{ij})\, C_{n,ij}}{R_{ij}^n} ,$$

where $f_n$ is a damping function, and $C_{n,ij}$ are heteroatomic dispersion coefficients are defined in terms of Hirshfeld-weighted atom-in-molecule polarizabilities and multipole moment integrals of the form

$$\left\langle M_\ell^2 \right\rangle_i = \sum_\sigma \int w_i(\boldsymbol{r})\, \rho_\sigma(\boldsymbol{r}) \left[ r_i^\ell - (r_i - d_{\text{XC}\sigma}(\boldsymbol{r}))^\ell \right]^2 \mathrm{d}\boldsymbol{r} .$$

$d_{\text{XC}\sigma}(\boldsymbol{r})$ is the XC-hole dipole moment, obtained by supplementing $d_{\text{X}}$ with same-spin ($\sigma\sigma$) and opposite-spin ($\sigma\sigma'$) correlation holes,

$$d_{\text{XC}\sigma} = \left( \int h_{\text{XC}\sigma}\, s\, d\boldsymbol{s} \right) - \boldsymbol{r} = b_\sigma + \left[ \frac{g_{\sigma\sigma}\, z_{\sigma\sigma}^7}{2 + z_{\sigma\sigma}} D_\sigma \right] + \left[ \frac{g_{\sigma\sigma'}\, z_{\sigma\sigma'}^5}{1 + z_{\sigma\sigma'}} \rho_{\sigma'} \right] - \boldsymbol{r} .$$

The BJ-damping function, defined in terms of the "critical" interatomic distance at which successive dispersion energy terms become equal, and Z-damping, defined in terms of the atomic numbers, are given by

$$f_n^{\text{BJ}}(R_{ij}) = \frac{R_{ij}^n}{R_{ij}^n + (a_1 R_{c,ij} + a_2)^n} , \qquad f_n^{\text{Z}}(R_{ij}) = \frac{R_{ij}^n}{R_{ij}^n + z_{\text{damp}} \frac{C_{n,ij}}{Z_i + Z_j}} .$$

The $a_1$, $a_2$, and $z_{\text{damp}}$ parameters are optimised by minimising the RMS percent error in binding energies for a set of 49 molecular dimers.

## WTMAD-4, GMTKN55, and Solid-state Benchmarks

Our analysis identified a flaw with the WTMAD-2, causing it to give subsets such as IL16 and DIPCS10 hundreds of times less weight than others, like BH76. We introduce WTMAD-4, which uses expected errors rather than energy scales for weighting, resulting in more balanced benchmark contributions.

$$\text{WTMAD-4} = \frac{1}{N_{\text{bench}}} \sum_{i=1}^{N_{\text{bench}}} w_i^{\text{WTMAD-4}} \cdot \text{MAD}_i$$

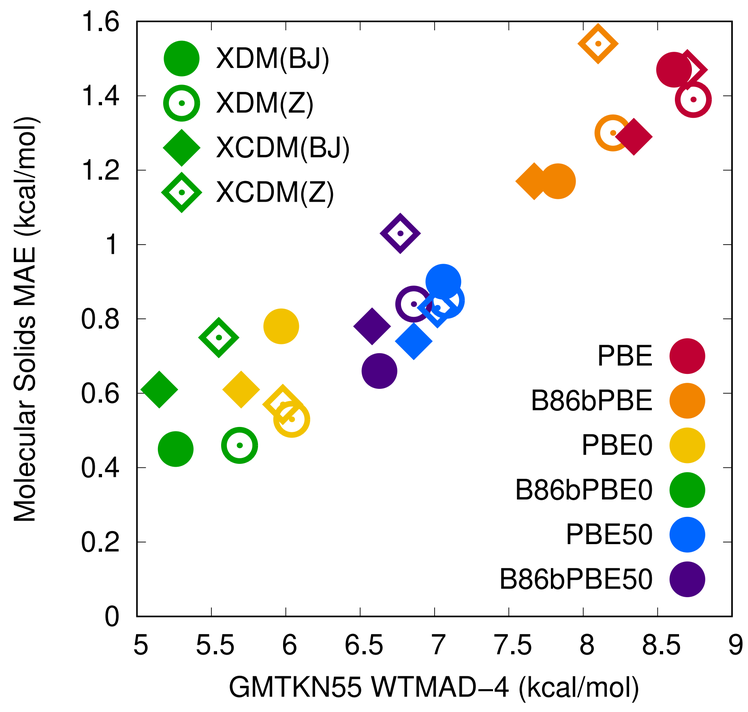
$$w_i = \begin{cases} 50 & \text{ACONF, RG18} \\ 25 & \text{ADIM6, Amino20x4, BUT14DIOL, HEAVY28, ICONF, MCONF, S66} \\ 10 & \text{BHROT27, HAL59, IL16, PCONF21, PNICO23, RSE43, S22, SCONF, UPU23} \\ 5 & \text{AHB21, CARBHB12, CDIE20, CHB6, ISO34, PArel, TAUT15} \\ 2.5 & \text{AL2X6, BH76, BH76RC, BHPERI, BSR36, FH51, G21EA, HEAVYSB11, IDISP, INV24, ISOL24, NBPRC, PA26, YBDE18} \\ 1 & \text{ALK8, ALKBDE10, BHDIV10, DARC, DIPCS10, G21IP, G2RC, PX13, RC21, W4-11, WATER27, WCPT18} \\ 0.5 & \text{C60ISO, DC13, MB16-43, SIE4x4} \end{cases}$$

GMTKN55 weighted MAD values (kcal/mol) for selected functionals and DCs:

| Functional | DC | WTMAD-2 | WTMAD-4 |
|---|---|---|---|
| PBE0 | D3(BJ) | 6.60 | 5.87 |
| PBE0 | TS | 6.53 | 6.43 |
| PBE0 | MBDrsSCS | 6.45 | 6.12 |
| PBE0 | MBD-NL | 6.53 | 6.16 |
| PBE0 | XDM(BJ) | 6.55 | 6.06 |
| PBE0 | XDM(Z) | 6.96 | 6.12 |
| PBE0 | XCDM(BJ) | **6.23** | **5.79** |
| PBE0 | XCDM(Z) | 6.88 | 6.06 |
| B86bPBE0 | XDM(BJ) | 5.78 | 5.34 |
| B86bPBE0 | XDM(Z) | 6.43 | 5.73 |
| B86bPBE0 | XCDM(BJ) | **5.59** | **5.23** |
| B86bPBE0 | XCDM(Z) | 6.29 | 5.60 |
| LC-$\omega$PBE | XDM(BJ) | 5.48 | 5.98 |
| LC-$\omega$PBE | XDM(Z) | 5.51 | 5.92 |
| LC-$\omega$PBE | XCDM(BJ) | 5.67 | 6.20 |
| LC-$\omega$PBE | XCDM(Z) | **5.44** | **5.85** |

As shown, XCDM(BJ) is the most accurate dispersion correction paired with PBE0, and B86b exchange outperforms PBE, confirming the importance of the large-gradient limit. B86bPBE0-XCDM(BJ) and LC-$\omega$PBE-XCDM(Z) appear best overall.

We also consider the X23, ICE13-Abs, ICE13-Rel, and HalCrys4 molecular crystal benchmarks. XCDM(BJ) achieved very low MAEs of 0.50–0.65 kcal/mol for all GGA and hybrid functionals tested using the `lightdenser` basis on X23, hinting at its use for CSP.




## References

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