

## INTRODUCTION AND MOTIVATION

Density-functional theory (DFT) allows first-principles computational modelling of the electronic structure of large-scale quantum systems. The combination of DFT's high efficiency and accuracy has positioned it as the workhorse of computational chemistry in recent years. Standard DFT methods neglect dispersion, a weak intermolecular force that determines properties like friction, adhesion, crystal structure packing, and the shapes of biomolecules. To capture dispersion interac-

tions, we incorporate corrections such as the exchange-hole dipole moment (XDM) model [1]. In recent studies, we demonstrated that XDM correctly captures dispersion physics and exhibits best-in-class performance on a benchmark of 15,000 chemical systems [2, 3]. Rather than using exact exchange, most implementations of the XDM model use the localized Becke-Roussel (BR) hole to calculate the exchange-hole dipole moments. This choice of model hole is more computationally efficient, especially for

solid-state systems, while also capturing non-dynamical correlation from chemical bonding, thereby improving accuracy for many molecular systems. However, this approach fails to capture short-range dynamical correlation, which we now add using the real-space model of Becke [4, 5]. Here, we present the mathematical framework, implementation in FHI-aims, and benchmarking of the exchange-correlation-hole dipole moment model (XCDM).

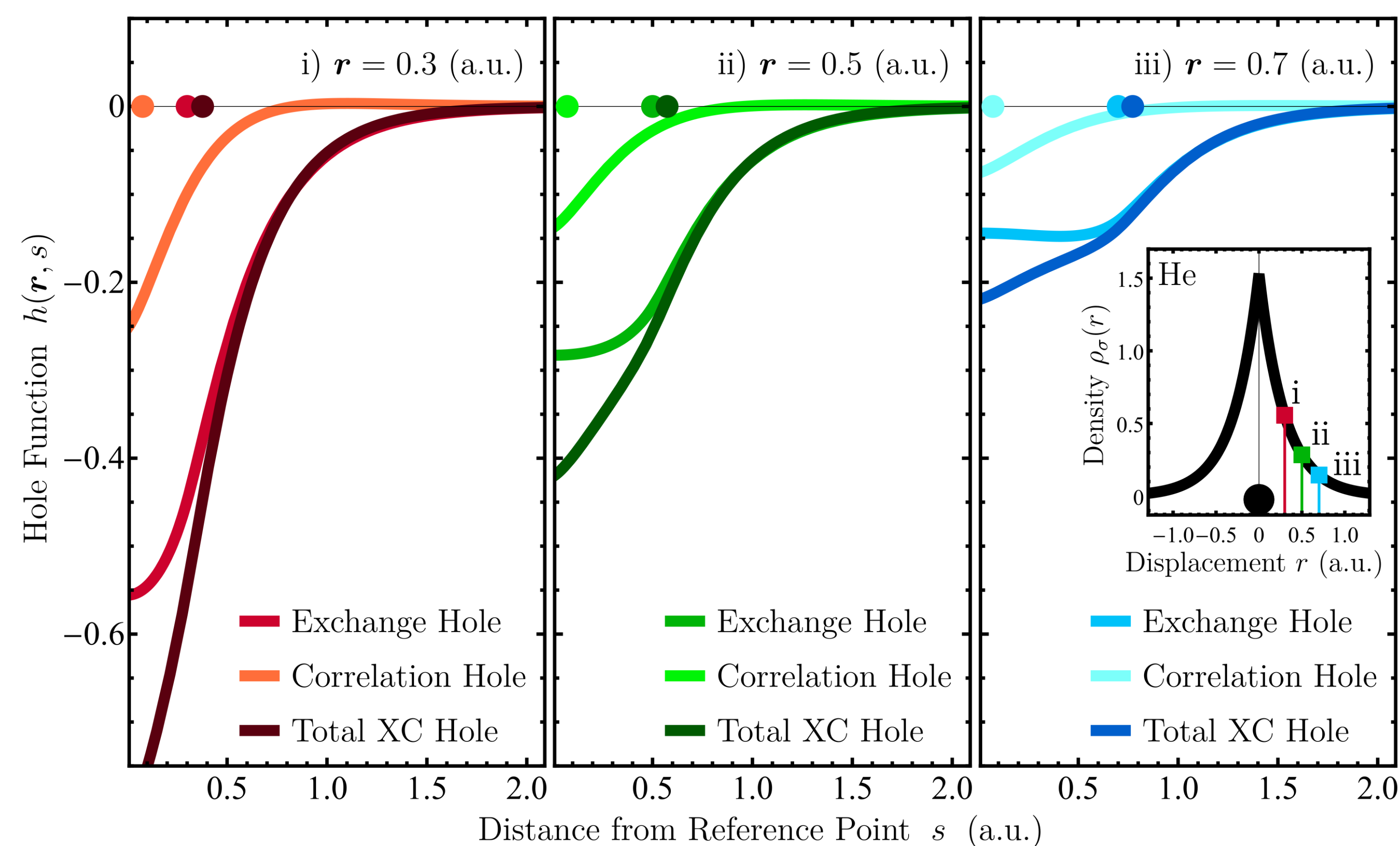
## XDM vs. XCDM BENCHMARK RESULTS

We compare the previous XDM implementation to the proposed XCDM variant for two important benchmarks: the X23 set of molecular crystal structures and a subset of S30L (S11L) that features supramolecular complexes with molecules of up to 160 atoms, non-polar dispersion, hydrogen bonding,  $\pi$ -stacked structures, and charged species. Calculations were performed in FHI-aims using a variety of common GGA and hybrid functionals paired with LightDense (light basis with tight integration grids) and Tight settings. The table below reports the mean absolute errors (MAEs) in energy (kcal/mol) for these benchmarks. The results show modest improvements in X23 and notable improvements in S11L as the original XDM method slightly underbinds while XCDM captures extra dispersion energy due to the inclusion of correlation.

Functional	X23				S11L			
	LightDense		Tight		LightDense		Tight	
	XDM	XCDM	XDM	XCDM	XDM	XCDM	XDM	XCDM
PBE	1.13	1.09	1.11	1.07	3.12	2.97	3.22	3.07
HSE06	1.15	1.11	—	—	1.10	1.00	1.36	1.24
PBE0	1.09	1.05	0.98	0.94	0.96	0.86	1.29	1.17
PBE-50	1.08	1.05	0.85	0.82	1.63	1.71	0.98	1.01
B86bPBE	0.83	0.81	0.70	0.68	1.25	1.16	1.07	1.02
B86bPBE-25	0.79	0.76	0.47	0.45	1.21	1.32	0.62	0.74
B86bPBE-50	0.91	0.88	0.52	0.52	2.55	2.66	1.83	1.97

## 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  $s$ . We see that, while the exchange hole approximates the total XC hole, the correlation contribution is non-negligible. On each plot's  $x$ -axis, the values of the opposite-spin correlation-hole dipole moment, the exchange-hole dipole moment, and their sum are noted.



## CORRELATION HOLE IMPLEMENTATION

The XDM model calculates the dispersion energy via

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

which sums over all atom pairs,  $i$  and  $j$ , and uses the Becke-Johnson damping function,  $f_n^{\text{BJ}}(R_{ij})$ . The  $C_{n,ij}$  heteroatomic dispersion coefficients are defined in terms of atom-in-molecule polarizabilities, and multipole ( $\ell$ -pole) moment integrals of the form

$$\langle M_\ell^2 \rangle_i = \sum_\sigma \int w_i(\mathbf{r}) \rho_\sigma(\mathbf{r}) [r_i^\ell - (r_i - d_{X\sigma}(\mathbf{r}))^\ell]^2 d\mathbf{r}.$$

Here,  $\rho_\sigma(\mathbf{r})$  is the electron density for spin state  $\sigma$ ,  $w_i(\mathbf{r})$  is the Hirshfeld weight, and  $d_{X\sigma}(\mathbf{r})$  is the exchange-hole dipole moment that we want to replace with the exchange-correlation-hole dipole moment:  $d_{XC\sigma}(\mathbf{r})$ . The total XC hole can be written as the sum of the same-spin ( $\sigma\sigma$ ) and opposite-spin ( $\alpha\beta$ ) correlation holes with the exchange hole,

$$d_{XC\sigma}(\mathbf{r}) = \left[ \int h_{XC}(\mathbf{r}, \mathbf{s}) s d\mathbf{s} \right] - \mathbf{r} = \left[ \int \left( h_{X\sigma} + h_{C\sigma}^{\sigma\sigma} + h_{C\sigma}^{\alpha\beta} \right) s d\mathbf{s} \right] - \mathbf{r}.$$

$d_{X\sigma}(\mathbf{r})$  is currently captured via the framework of the BR hole, which we can leverage to capture  $d_{XC\sigma}(\mathbf{r})$ . Becke proposed analogous models for the same- and opposite-spin correlation holes of the form [4, 5]

$$h_{C\sigma}^{\sigma\sigma}(\mathbf{r}, \mathbf{s}) = \frac{s^2 (s - z_{\sigma\sigma}) D_\sigma(\mathbf{r})}{3(2 + z_{\sigma\sigma})} (1 + \gamma_{\sigma\sigma} s) e^{-\gamma_{\sigma\sigma} s},$$

$$h_{C\sigma}^{\alpha\beta}(\mathbf{r}, \mathbf{s}) = \frac{(s - z_{\alpha\beta}) \rho_\sigma(\mathbf{r})}{1 + z_{\alpha\beta}} (1 + \gamma_{\alpha\beta} s) e^{-\gamma_{\alpha\beta} s},$$

where  $s$  is the reference point,  $z$  is the spin-dependent correlation length (obtainable from the BR model),  $\gamma$  is a coefficient that ensures the correlation holes normalize to zero electrons, and  $D_\sigma(\mathbf{r}) = \tau_\sigma(\mathbf{r}) - \tau_\sigma^{\text{W}}(\mathbf{r})$  is the difference between the exact kinetic-energy density and the von Weizsäcker approximation. Spherical integration of these hole functions yields the following dipole-moment contributions,

$$d_{C\sigma}^{\sigma\sigma}(\mathbf{r}) = \left[ \int h_{C\sigma}^{\sigma\sigma}(\mathbf{r}, \mathbf{s}) s d\mathbf{s} \right] - \mathbf{r} = \frac{c_{\sigma\sigma} z_{\sigma\sigma}^7 D_\sigma(\mathbf{r})}{2 + z_{\sigma\sigma}} - \mathbf{r},$$

$$d_{C\sigma}^{\alpha\beta}(\mathbf{r}) = \left[ \int h_{C\sigma}^{\alpha\beta}(\mathbf{r}, \mathbf{s}) s d\mathbf{s} \right] - \mathbf{r} = \frac{c_{\alpha\beta} z_{\alpha\beta}^5 \rho_\sigma(\mathbf{r})}{1 + z_{\alpha\beta}} - \mathbf{r}.$$

## FURTHER READING

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