



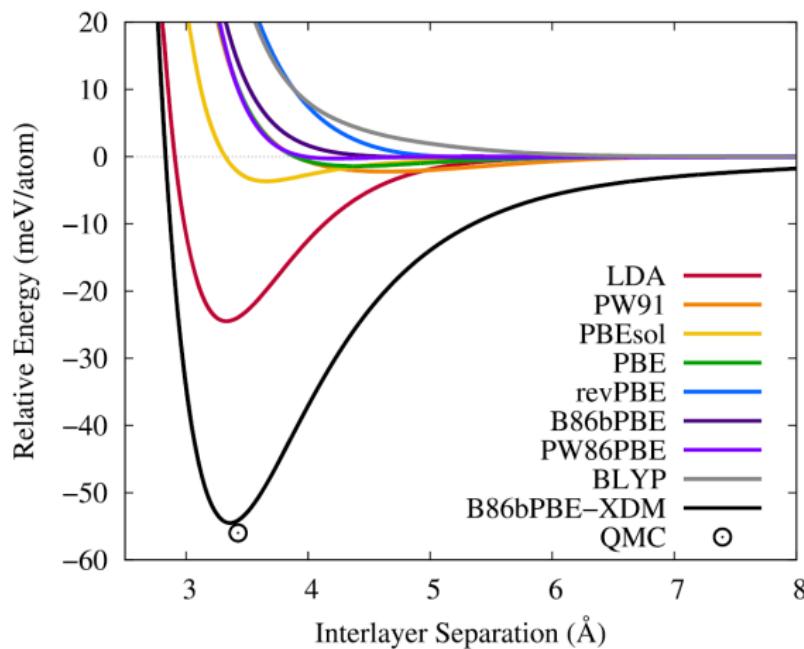
## CAPTURING MANY-BODY DISPERSION WITH EXCHANGE-HOLE DIPOLES



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## DISPERSION IN DFT

EXAMPLE: SEPARATING GRAPHITE LAYERS



## ELECTRONIC MANY-BODY EFFECTS

Refers to changes in the pairwise dispersion coefficients due to changes in the atomic environment.

$$E_{\text{Disp}}^{(2)} = - \sum_{i < j} \left[ \frac{C_{6,ij}}{R_{ij}^6} + \frac{C_{8,ij}}{R_{ij}^8} + \frac{C_{10,ij}}{R_{ij}^{10}} + \dots \right]$$

## ATOMIC MANY-BODY EFFECTS

Refer to terms in the perturbation-theory expansion of the dispersion energy that involve more than two atoms.

$$E_{\text{Disp}}^{(3)} = - \sum_{i < j < k} \frac{C_{9,ijk} [3 \cos(\theta_i) \cos(\theta_j) \cos(\theta_k) + 1]}{R_{ij}^3 R_{jk}^3 R_{ki}^3}$$

## THE EXCHANGE-HOLE DIPOLE MOMENT (XDM) MODEL

Multipole moment integrals are computed for each particle, and are then used to generate the  $C_{n,ij}^{\text{XDM}}$  dispersion coefficients.

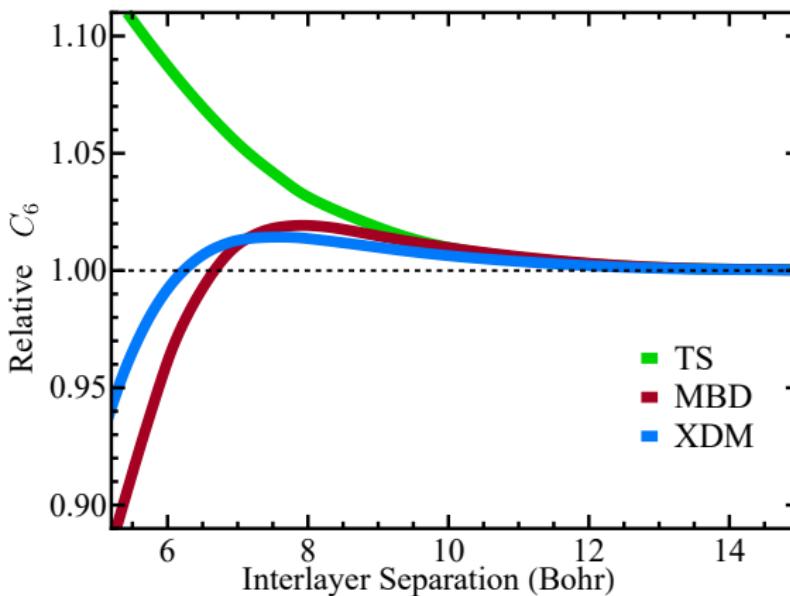
$$E_{\text{XDM}} = - \sum_{i < j} \left[ \frac{C_{6,ij}^{\text{XDM}} f_6^{\text{BJ}}(R_{ij})}{R_{ij}^6} + \frac{C_{8,ij}^{\text{XDM}} f_8^{\text{BJ}}(R_{ij})}{R_{ij}^8} + \frac{C_{10,ij}^{\text{XDM}} f_{10}^{\text{BJ}}(R_{ij})}{R_{ij}^{10}} \right]$$

## THE MANY-BODY DISPERSION (MBD) MODEL

The system is replaced with a coupled fluctuating dipole model (CFDM) Hamiltonian to calculate the difference between coupled and uncoupled states.

$$E_{\text{MBD}} = \frac{1}{2} \sum_{i=1}^{3N} \sqrt{\lambda_i^{\text{CFDM}}} - \frac{3}{2} \sum_{i=1}^N \omega_i^{\text{SCS}}$$

## COMPARISON BETWEEN XDM AND MBD



XDM and MBD behave similarly for graphite.

We want to compare these two models on harmonic oscillator systems

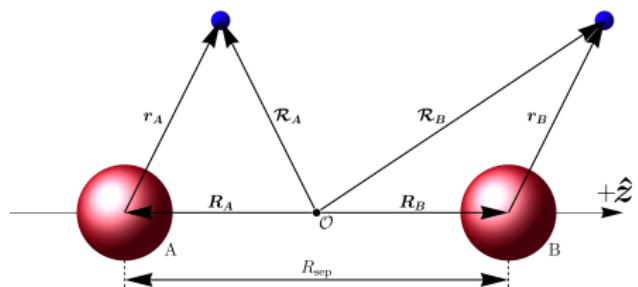
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Adapted with permission from:

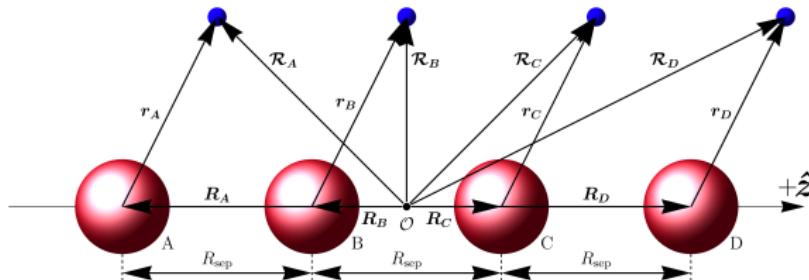
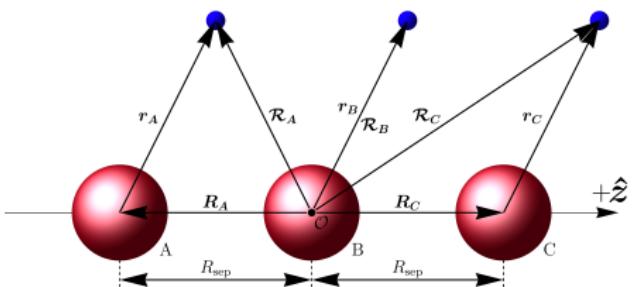
Otero-de-la-Roza, A. et al. *J. Phys. Chem. Lett.*, **11** 6, 2298–2302. (2020) doi: 10.1021/acs.jpclett.0c00348

## SYSTEM GEOMETRY

DIMER



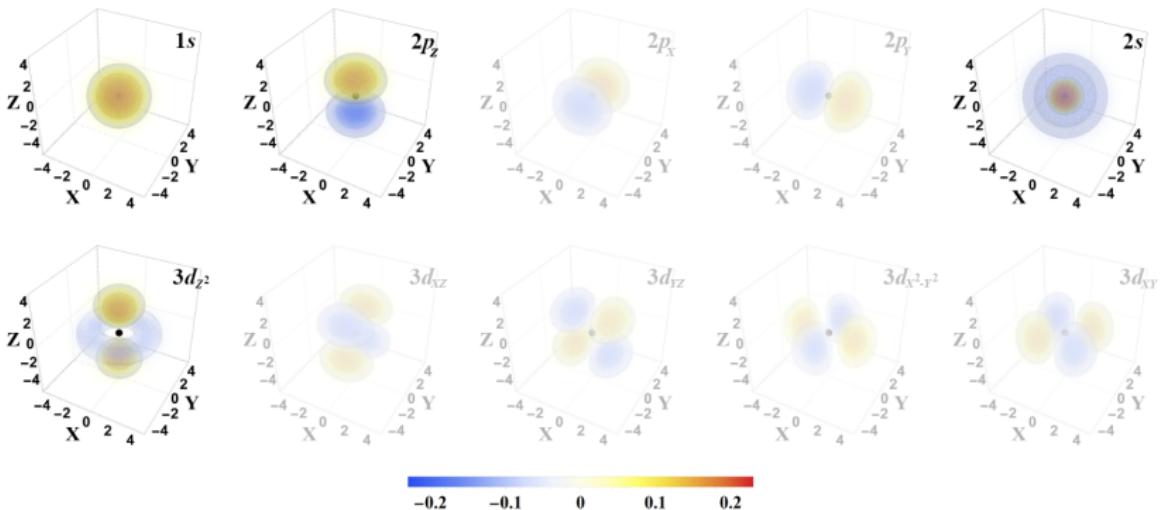
TRIMER



TETRAMER

## HAMILTONIAN AND WAVEFUNCTIONS

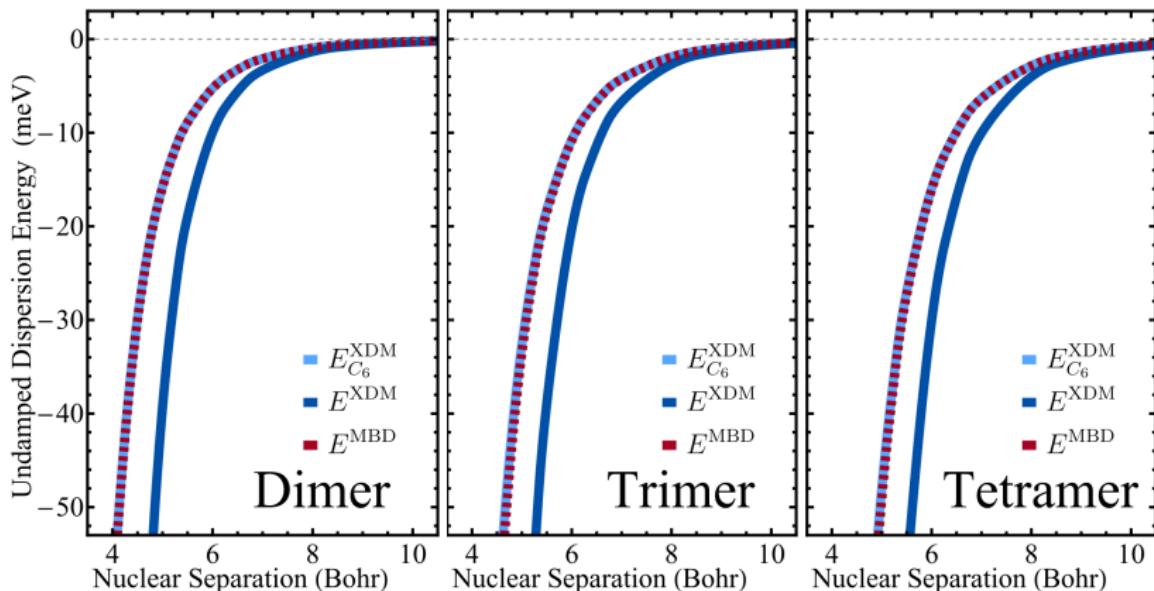
$$\hat{H} = \sum_p \hat{H}_p^{\text{NI}} + \sum_{q \neq p} \left( \hat{H}_{pq}^{\text{e-nuc}} + \frac{1}{2} \hat{H}_{pq}^{\text{e-e}} \right) + E_{\text{total}}^{\text{nuc-nuc}}$$



$$\mathbf{X}(\mathbf{r}) = \sum_i c_i \chi_i(\mathbf{r})$$

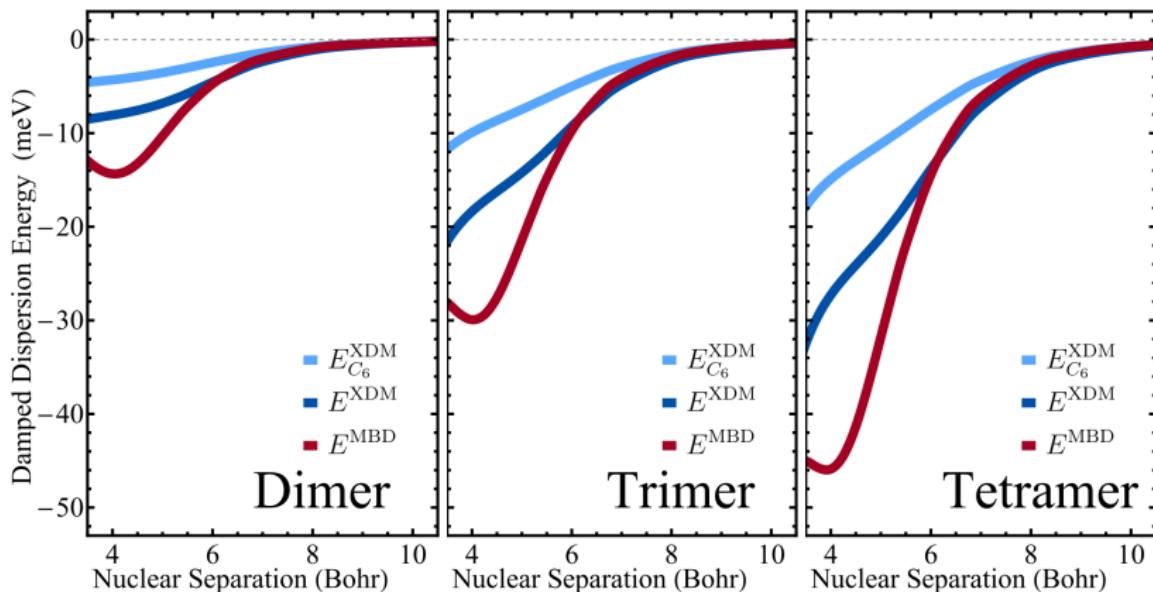
$$\sum_i c_i^2 = 1$$

## UNDAMPED ENERGY COMPARISON

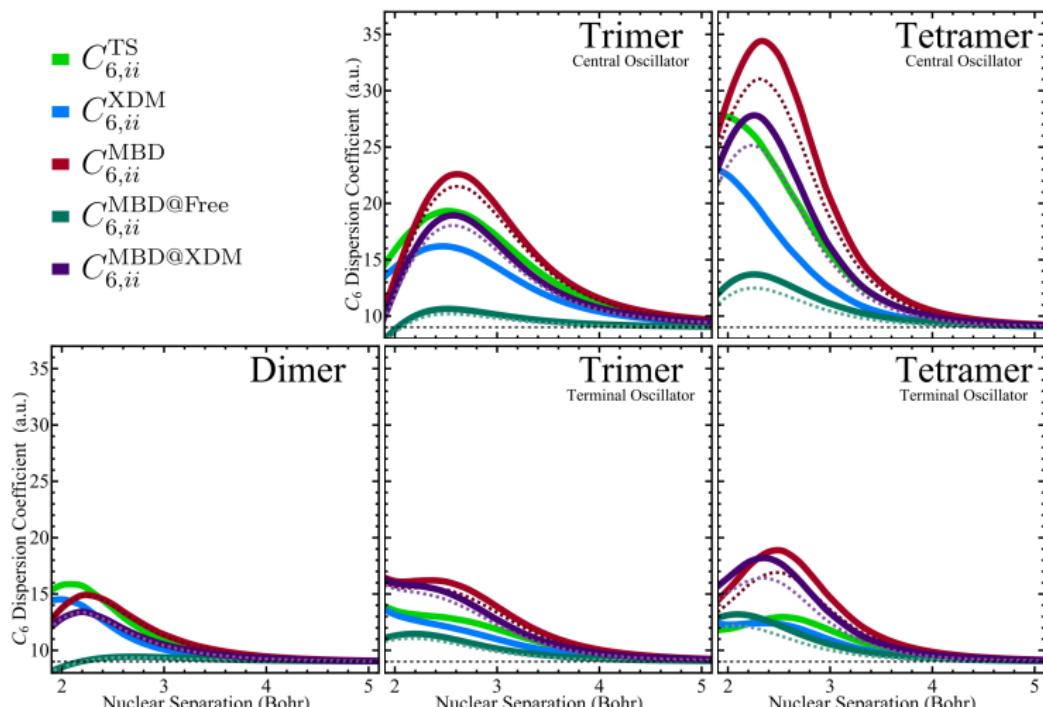


MBD seems to only account for first-order corrections to the dispersion energy ( $C_6$ ), while XDM accounts for higher-order effects ( $C_8, C_{10}$ ).

## DAMPED ENERGY COMPARISON

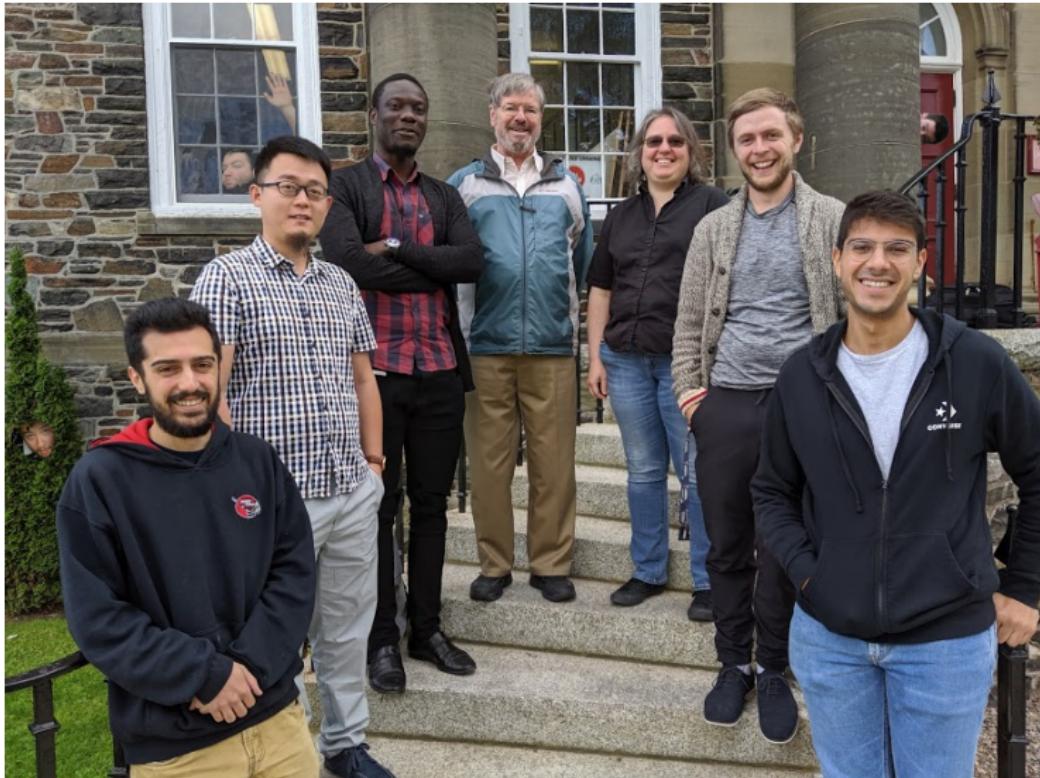


We optimized both XDM and MBDs damping parameters on noble gas dimers. MBD has weaker damping, allowing it to emulate higher-order behaviour.

COMPARISON OF  $C_6$  DISPERSION COEFFICIENTS

TS, MBD, and XDM capture similar changes in  $C_6$  for these bonded systems.  
We are currently investigating if this is also the case for non-bonded systems.  
MBD seems to be sensitive to starting conditions.

# ACKNOWLEDGEMENTS



# QUESTIONS?

WANT MY SLIDES?



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## HOHENBERG-KOHN-SHAM DFT

Density-functional theory (DFT) has proven to be one of the most accurate ways of calculating the electronic structure of molecules and solids while maintaining sufficiently low computational requirements.

The  $N$ -electron problem is greatly simplified by writing the total energy,

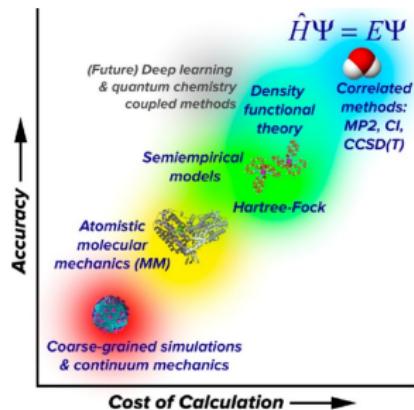
$$E[\rho] = T_s[\rho] + \int v_{\text{ext}}\rho(\mathbf{r})d\mathbf{r} + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho],$$

as a functional of the electron density,

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2$$

for  $N$  electrons occupying orbitals  $\psi_i(\mathbf{r})$ . Forces are calculated via the Hellmann-Feynman theorem

$$\mathbf{F}_r = - \left\langle \frac{\partial \hat{H}}{\partial \mathbf{r}} \right\rangle = - \frac{\partial E}{\partial \mathbf{r}}$$



Borges et al., *Chem. Rev.* **121** 10, 5633–5670. (2021) doi: 10.1021/acs.chemrev.0c00901

## THE TS MODEL

The Tkatchenko-Scheffler (TS) model only considers the lowest-order dispersion term, corresponding to instantaneous dipole-dipole contributions of the form

$$E_{\text{TS}} = - \sum_i \sum_{j < i} f^{\text{WY}}(R_{ij}) \frac{C_{6,ij}^{\text{TS}}}{R_{ij}^6},$$

where  $f^{\text{WY}}$  is a Wu-Yang damping function. The heteroatomic dispersion coefficients are obtained from their homoatomic counterparts using the Slater-Kirkwood formula:

$$C_{6,ij}^{\text{TS}} = \frac{2C_{6,ii}C_{6,jj}}{\frac{\alpha_j^0}{\alpha_i^0}C_{6,ii} + \frac{\alpha_i^0}{\alpha_j^0}C_{6,jj}}.$$

In the TS model, the homoatomic dispersion coefficients, static polarizabilities, and vdW radii are determined from their free values and effective volumes  $v_i = \langle r^3 \rangle_i$  as,

$$C_{6,ii}^{\text{free}} = \left( \frac{v_i}{v_i^{\text{free}}} \right)^2 C_{6,ii}^{\text{free}}, \quad \alpha_i^0 = \left( \frac{v_i}{v_i^{\text{free}}} \right) \alpha_i^{\text{free}}, \quad R_i = \left( \frac{v_i}{v_i^{\text{free}}} \right)^{\frac{1}{3}} R_i^{\text{free}}.$$

## THE XDM MODEL

The exchange-hole dipole moment (XDM) model calculates the dispersion energy via

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

using the Becke-Johnson damping function,  $f_n^{\text{BJ}}(R_{ij})$ , defined in terms of the van der Waals radius,  $R_{\text{vdW},ij} = (a_1 R_{c,ij} + a_2)$ , and the critical damping radius

$$f_n^{\text{BJ}} = \frac{R_{ij}^n}{R_{ij}^n + R_{\text{vdW},ij}^n}, \quad R_{c,ij} = \frac{1}{3} \left[ \left( \frac{C_{8,ij}^{\text{XDM}}}{C_{6,ij}^{\text{XDM}}} \right)^{\frac{1}{2}} + \left( \frac{C_{10,ij}^{\text{XDM}}}{C_{6,ij}^{\text{XDM}}} \right)^{\frac{1}{4}} + \left( \frac{C_{10,ij}^{\text{XDM}}}{C_{8,ij}^{\text{XDM}}} \right)^{\frac{1}{2}} \right]$$

The multipole moment integral is defined in terms of the Hirshfeld weights and the exchange-hole dipole moment

$$\langle M_\ell^2 \rangle = \sum_\sigma \int w_i(\mathbf{r}) \rho_\sigma(\mathbf{r}) \left[ r^\ell - (r - d_{X,\sigma})^\ell \right]^2 d\mathbf{r},$$

which is then used to solve for the heteroatomic dispersion coefficients,  $C_{n,ij}^{\text{XDM}}$ .

## THE MBD MODEL

The many-body dispersion (MBD) model revolves around solving the coupled fluctuating dipole model (CFDM) Hamiltonian

$$\hat{H} = -\frac{1}{2} \sum_i^N \nabla_{\xi_i}^2 + \frac{1}{2} \sum_i^N \left( \omega_i^{SCS} \xi_i \right)^2 + \sum_i^N \sum_{j < i}^N \omega_i^{SCS} \omega_j^{SCS} \sqrt{\alpha_i^{SCS} \alpha_j^{SCS}} \xi_i \mathbf{T}'_{ij} \xi_j ,$$

which uses parameters that have been refined through the self-consistent screening (SCS) equation

$$\alpha_i^{SCS}(i\omega) = \alpha_i^{TS}(i\omega) + \alpha_i^{TS}(i\omega) \sum_{j \neq i} \mathbf{T}_{ij} \alpha_j^{SCS}(i\omega) .$$

The CFDM eigenvalues and SCS excitation frequencies are used to calculate the MBD energy

$$E_{MBD} = \frac{1}{2} \sum_{i=1}^{3N} \sqrt{\lambda_i} - \frac{3}{2} \sum_{i=1}^N \omega_i^{SCS} .$$

## WAVEFUNCTIONS

We start by solving the isotropic quantum harmonic oscillator

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 + \frac{1}{2}\mu\omega^2r^2 \quad E = \hbar\omega\left(2k + \ell + \frac{3}{2}\right) \quad n = 2k + \ell$$

with eigenvector solutions given by

$$\chi_{k\ell m}(r, \theta, \phi) = N_{k\ell} r^\ell e^{-\nu r^2} L_k^{\ell+\frac{1}{2}}(2\nu r^2) Y_\ell^m(\theta, \phi) \quad \nu = \mu\omega/2\hbar$$

We take a linear combination of wavefunctions

$$X(\mathbf{r}) = \sum_i c_i \chi_i(\mathbf{r}) \quad \sum_i c_i^2 = 1$$

for use in the dimer and trimer systems of interest.

## ENERGY EXPRESSION

$$\hat{H}_{\text{total}} = \sum_p \hat{H}_p^{\text{NI}} + \sum_{p \neq q} \left( \hat{H}_{pq}^{\text{e-nuc}} + \frac{1}{2} \hat{H}_{pq}^{\text{e-e}} \right) + E_{\text{total}}^{\text{nuc-nuc}}$$

## DIMER AND TRIMER HAMILTONIANS

$$\hat{H}_{\text{dimer}} = \hat{H}_A^{\text{NI}} + \hat{H}_B^{\text{NI}} + \hat{H}_{AB}^{\text{e-nuc}} + \hat{H}_{BA}^{\text{e-nuc}} + \frac{1}{2} \left( \hat{H}_{AB}^{\text{e-e}} + \hat{H}_{BA}^{\text{e-e}} \right) + E_{\text{total}}^{\text{nuc-nuc}}$$

$$\begin{aligned} \hat{H}_{\text{trimer}} = & \hat{H}_A^{\text{NI}} + \hat{H}_B^{\text{NI}} + \hat{H}_C^{\text{NI}} \\ & + \hat{H}_{AB}^{\text{e-nuc}} + \hat{H}_{AC}^{\text{e-nuc}} + \hat{H}_{BA}^{\text{e-nuc}} + \hat{H}_{BC}^{\text{e-nuc}} + \hat{H}_{CA}^{\text{e-nuc}} + \hat{H}_{CB}^{\text{e-nuc}} \\ & + \frac{1}{2} \left( \hat{H}_{AB}^{\text{e-e}} + \hat{H}_{AC}^{\text{e-e}} + \hat{H}_{BA}^{\text{e-e}} + \hat{H}_{BC}^{\text{e-e}} + \hat{H}_{CA}^{\text{e-e}} + \hat{H}_{CB}^{\text{e-e}} \right) \\ & + E_{\text{total}}^{\text{nuc-nuc}} \end{aligned}$$

## ENERGY EXPRESSION

$$\hat{H}_{\text{total}} = \sum_p \hat{H}_p^{\text{NI}} + \sum_{p \neq q} \left( \hat{H}_{pq}^{\text{e-nuc}} + \frac{1}{2} \hat{H}_{pq}^{\text{e-e}} \right) + E_{\text{total}}^{\text{nuc-nuc}}$$

## NON-INTERACTING COMPONENT

$$\begin{aligned}\langle \hat{H}_A^{\text{NI}} \rangle &= \left\langle \sum_i c_i \chi_{A,i} \middle| \hat{H}_A^{\text{NI}} \middle| \sum_j c_j \chi_{A,j} \right\rangle \\ &= \sum_{ij} c_i c_j \delta_{ij} \left\langle \chi_{A,i} \middle| -\frac{\hbar^2}{2\mu_A} \nabla_A^2 + \frac{1}{2} \mu_A \omega_A^2 r_A^2 \middle| \chi_{A,j} \right\rangle \\ &= \sum_i c_i^2 \left\langle \chi_{A,i} \middle| -\frac{\hbar^2}{2\mu_A} \nabla_A^2 + \frac{1}{2} \mu_A \omega_A^2 r_A^2 \middle| \chi_{A,i} \right\rangle\end{aligned}$$

## ENERGY EXPRESSION

$$\hat{H}_{\text{total}} = \sum_p \hat{H}_p^{\text{NI}} + \sum_{p \neq q} \left( \hat{H}_{pq}^{\text{e-nuc}} + \frac{1}{2} \hat{H}_{pq}^{\text{e-e}} \right) + E_{\text{total}}^{\text{nuc-nuc}}$$

## ELECTRON-NUCLEAR COMPONENT

$$\begin{aligned} \langle \hat{H}_{AB}^{\text{e-nuc}} \rangle &= \left\langle \sum_i c_i \chi_{A,i} \left| \hat{H}_{AB}^{\text{e-nuc}} \right| \sum_j c_j \chi_{A,j} \right\rangle \\ &= \sum_{ij} c_i c_j \left\langle \chi_{A,i} \left| \frac{e^2}{4\pi\epsilon_0} \frac{-Z_B}{|\boldsymbol{\mathcal{R}}_A - \boldsymbol{R}_B|} \right| \chi_{A,j} \right\rangle \end{aligned}$$

## ENERGY EXPRESSION

$$\hat{H}_{\text{total}} = \sum_p \hat{H}_p^{\text{NI}} + \sum_{p \neq q} \left( \hat{H}_{pq}^{\text{e-nuc}} + \frac{1}{2} \hat{H}_{pq}^{\text{e-e}} \right) + E_{\text{total}}^{\text{nuc-nuc}}$$

## ELECTRON-ELECTRON COMPONENT

$$\begin{aligned} \left\langle \hat{H}_{AB}^{\text{e-e}} \right\rangle &= \frac{1}{2} \left\langle \sum_{i_1} c_{i_1} \chi_{A,i_1} \sum_{i_2} d_{i_2} \chi_{B,i_2} \left| \hat{H}_{AB}^{\text{e-e}} \right| \sum_{i_3} c_{i_3} \chi_{A,i_3} \sum_{i_4} d_{i_4} \chi_{B,i_4} \right\rangle \\ &= \frac{1}{2} \sum_{i_1 i_2 i_3 i_4} c_{i_1} d_{i_2} c_{i_3} d_{i_4} \left\langle \chi_{A,i_1} \chi_{B,i_2} \left| \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathcal{R}_A - \mathcal{R}_B|} \right| \chi_{A,i_3} \chi_{B,i_4} \right\rangle \end{aligned}$$

## ENERGY EXPRESSION

$$\hat{H}_{\text{total}} = \sum_p \hat{H}_p^{\text{NI}} + \sum_{p \neq q} \left( \hat{H}_{pq}^{\text{e-nuc}} + \frac{1}{2} \hat{H}_{pq}^{\text{e-e}} \right) + E_{\text{total}}^{\text{nuc-nuc}}$$

## NUCLEAR-NUCLEAR COMPONENT

$$E_{\text{total}}^{\text{nuc-nuc}} = \sum_p \sum_{q < p} \frac{e^2}{4\pi\epsilon_0} \frac{Z_p Z_q}{|\mathbf{R}_p - \mathbf{R}_q|}$$

## VARIATIONAL MINIMIZATION

$$\hat{H} = \sum_p \hat{H}_p^{\text{NI}} + \sum_{q \neq p} \left( \hat{H}_{pq}^{\text{e-nuc}} + \frac{1}{2} \hat{H}_{pq}^{\text{e-e}} \right) + E_{\text{total}}^{\text{nuc-nuc}}$$

Minimizing  $\langle \hat{H} \rangle$  is a constrained optimization problem, suitable for the method of Lagrange multipliers. The Lagrangian of our two systems are determined by

$$\mathcal{L}(\{c_i\}, \lambda) = \langle \hat{H}_{\text{dimer}} \rangle - \lambda \left( 1 - \sum_i c_i^2 \right)$$

$$\mathcal{L}(\{c_i\}, \{d_i\}, \lambda_1, \lambda_2) = \langle \hat{H}_{\text{trimer}} \rangle - \lambda_1 \left( 1 - \sum_i c_i^2 \right) - \lambda_2 \left( 1 - \sum_i d_i^2 \right)$$

The critical points on our potential energy surface may be found by solving for the expansion coefficients,  $\{c_i\}$  and  $\{d_i\}$ , in the equations generated by

$$\nabla \mathcal{L} = 0.$$

## IMPLEMENTATION OF MBD

To implement MBD, we need to derive “MBD”  $C_6$  coefficients. To do that, we need to solve for the SCS polarizabilities

$$\alpha_i^{\text{SCS}}(i\omega) = \alpha_i^{\text{TS}}(i\omega) + \alpha_i^{\text{TS}}(i\omega) \sum_{j \neq i} \mathbf{T}_{ij} \boldsymbol{\alpha}_j^{\text{SCS}}(i\omega)$$

where the TS polarizabilities are

$$\alpha_i^{\text{TS}}(\omega) = \frac{\alpha_i^0}{1 - (\omega/\omega_i)^2}$$

$\mathbf{T} = \nabla_{\mathbf{R}_i} \otimes \nabla_{\mathbf{R}_j} v_{ij}$  is a fourth-rank (modified) dipole-dipole interaction tensor. Thankfully, we have the form of its elements as used in MBD:

$$\begin{aligned} \mathcal{T}_{ij}^{ab} &= -\frac{3\mathbf{R}_a \mathbf{R}_b - R_{ij}^2 \delta_{ab}}{R_{ij}^5} \left( \operatorname{erf} \left[ \frac{R_{ij}}{\sigma_{ij}} \right] - \frac{2}{\sqrt{\pi}} \frac{R_{ij}}{\sigma_{ij}} e^{-R_{ij}^2/\sigma_{ij}^2} \right) \\ &\quad + \frac{4}{\sqrt{\pi}} \frac{\mathbf{R}_a \mathbf{R}_b}{\sigma_{ij}^3 R_{ij}^3} e^{-R_{ij}^2/\sigma_{ij}^2} \end{aligned}$$

## IMPLEMENTATION OF MBD

To implement MBD, one can construct a  $3N \times 3N$  matrix,  $\mathbf{A}$ , which is partitioned by  $3 \times 3$  sub-blocks representing each atom pair in the system.

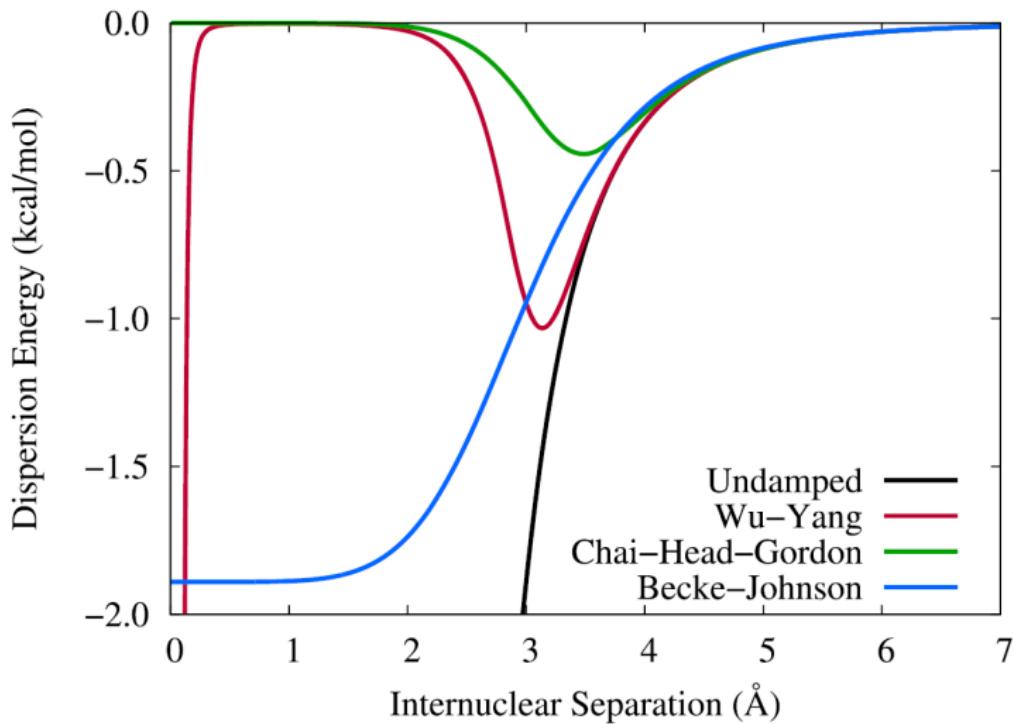
$$\mathbf{A} = \begin{bmatrix} 1/\alpha_1^{\text{TS}} & 0 & 0 & \mathcal{T}_{12}^{xx} & \mathcal{T}_{12}^{xy} & \mathcal{T}_{12}^{xz} & \mathcal{T}_{13}^{xx} & \mathcal{T}_{13}^{xy} & \mathcal{T}_{13}^{xz} \\ 0 & 1/\alpha_1^{\text{TS}} & 0 & \mathcal{T}_{12}^{yx} & \mathcal{T}_{12}^{yy} & \mathcal{T}_{12}^{yz} & \mathcal{T}_{13}^{yx} & \mathcal{T}_{13}^{yy} & \mathcal{T}_{13}^{yz} \\ 0 & 0 & 1/\alpha_1^{\text{TS}} & \mathcal{T}_{12}^{zx} & \mathcal{T}_{12}^{zy} & \mathcal{T}_{12}^{zz} & \mathcal{T}_{13}^{zx} & \mathcal{T}_{13}^{zy} & \mathcal{T}_{13}^{zz} \\ \hline \mathcal{T}_{21}^{xx} & \mathcal{T}_{21}^{xy} & \mathcal{T}_{21}^{xz} & 1/\alpha_2^{\text{TS}} & 0 & 0 & \mathcal{T}_{23}^{xx} & \mathcal{T}_{23}^{xy} & \mathcal{T}_{23}^{xz} \\ \mathcal{T}_{21}^{yx} & \mathcal{T}_{21}^{yy} & \mathcal{T}_{21}^{yz} & 0 & 1/\alpha_2^{\text{TS}} & 0 & \mathcal{T}_{23}^{yx} & \mathcal{T}_{23}^{yy} & \mathcal{T}_{23}^{yz} \\ \mathcal{T}_{21}^{zx} & \mathcal{T}_{21}^{zy} & \mathcal{T}_{21}^{zz} & 0 & 0 & 1/\alpha_2^{\text{TS}} & \mathcal{T}_{23}^{zx} & \mathcal{T}_{23}^{zy} & \mathcal{T}_{23}^{zz} \\ \hline \mathcal{T}_{31}^{xx} & \mathcal{T}_{31}^{xy} & \mathcal{T}_{31}^{xz} & \mathcal{T}_{32}^{xx} & \mathcal{T}_{32}^{xy} & \mathcal{T}_{32}^{xz} & 1/\alpha_3^{\text{TS}} & 0 & 0 \\ \mathcal{T}_{31}^{yx} & \mathcal{T}_{31}^{yy} & \mathcal{T}_{31}^{yz} & \mathcal{T}_{32}^{yx} & \mathcal{T}_{32}^{yy} & \mathcal{T}_{32}^{yz} & 0 & 1/\alpha_3^{\text{TS}} & 0 \\ \mathcal{T}_{31}^{zx} & \mathcal{T}_{31}^{zy} & \mathcal{T}_{31}^{zz} & \mathcal{T}_{32}^{zx} & \mathcal{T}_{32}^{zy} & \mathcal{T}_{32}^{zz} & 0 & 0 & 1/\alpha_3^{\text{TS}} \end{bmatrix}$$

Inverting  $\mathbf{A}$  permits quick computation of the SCS polarizability tensor,

$$\alpha_i^{\text{SCS}} = \sum_{j=1}^N [\mathbf{A}^{-1}]_{ij} .$$

The diagonal elements of  $\alpha_i^{\text{SCS}}$  may be substituted into the Casimir-Polder integral to determine the effective MBD  $C_6$  values.

## DAMPING FUNCTIONS



## OPTIMIZED DAMPING PARAMETERS

The XDM and MBD damping parameters were optimized on the KB65(6) subset of noble gas dimers of He, Ne, and Ar pairs.

PW86PBE was the most accurate of the functionals tested, and reaches the CBS limit at the quintuple-zeta level of theory.

XDM was parametrized by minimizing the RMSPD of CP-corrected PW86PBE-XDM/aug-pV5Z binding energies.

MBD's contribution was calculated using FHIaims with a 'tight' basis using the PBE functional.