

London Dispersion forces without Density Distortion: the Fixed Diagonal Matrices (FDM) method

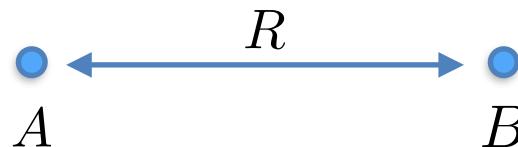
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1. DPK & P. Gori-Giorgi, *J. Phys. Chem. Lett.* **10** (7), 1537-1541 (2019) doi: [10.1021/acs.jpclett.9b00469](https://doi.org/10.1021/acs.jpclett.9b00469)
 2. DPK & P. Gori-Giorgi, *Faraday Discuss.*, **224**, 145-165 (2020) doi: [10.1039/D0FD00056F](https://doi.org/10.1039/D0FD00056F)
 3. DPK, T. Weckman & P. Gori-Giorgi, *J. Chem. Theory Comput.*, **17** (4), 2283-2293 (2021) doi: [10.1021/acs.jctc.1c00102](https://doi.org/10.1021/acs.jctc.1c00102)
- 3a. DPK. *Fixed Diagonal Matrices*. <https://github.com/DerkKooi/fdm>

What is dispersion?

- Consider two monomers A and B (atoms, molecules, nanodots):



$$E_{\text{int}}^{AB}(R) = E^{AB}(R) - E_0^A - E_0^B$$

- Now consider the limit of large separation:

$$E_{\text{int}}^{AB}(R) = \sum_{n=1}^{\infty} \frac{C_n}{R^n} + \mathcal{O}(R^M e^{-DR})$$

charge overlap and exchange

(induced) multipole -(induced) multipole interaction

Arrows point from the terms to their respective labels: the first term to "charge overlap and exchange", the second term to "(induced) multipole -(induced) multipole interaction".

- We expand the interaction in orders:

$$E_{\text{int}}^{AB}(R) = E_{\text{int}}^{(1)}(R) + E_{\text{int}}^{(2)}(R) + \dots$$

electrostatics: multipole-multipole ($\sim 1/R^3$)

induction+dispersion: ($\sim 1/R^6$)
(induced) multipole- induced multipole

Arrows point from the terms to their respective labels: the first term to "electrostatics: multipole-multipole ($\sim 1/R^3$)", the second term to "induction+dispersion: ($\sim 1/R^6$) (induced) multipole- induced multipole".

What is dispersion?

- Partition Hamiltonian:

$$\hat{H}(R) = \hat{H}_A + \hat{H}_B + \hat{H}_{\text{int}}(R)$$

Isolated systems

*Coulomb interaction between nuclei and electrons
on different systems*



- Now consider the limit of large separation:

$$\hat{H}_{\text{int}}(R) = \sum_{n=1}^{\infty} \frac{\hat{H}_{\text{int},n}}{R^n}$$

- Large R : isolated systems, Rayleigh-Schrödinger Perturbation Theory
- Polarisation approximation: ignore antisymmetry, Hilbert space: $H_{AB} = H_A \otimes H_B$, not $H_{AB} = H_A \wedge H_B$

Density Functional Theory

$$E_{\text{tot}}[v_{\text{ext}}] = \min_{\rho} \left(\int d\mathbf{r} \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) + F[\rho] \right)$$
$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle$$
$$F[\rho] = T_s[\rho] + U[\rho] + E_{\text{xc}}[\rho]$$
$$U[\rho] = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Dispersion

Electrostatics
and induction

- Problem for semi-local functionals (LDA, GGA, meta-GGA):

$$E_{\text{xc}}[\rho, R] = E_{\text{xc}}[\rho^A] + E_{\text{xc}}[\rho^B] + \mathcal{O}(e^{-AR})$$

- Same holds for hybrids (but not for double hybrids)

$$E_{\text{xc}}[\rho] = E_{\text{xc},sl/hyb}[\rho] + E_{\text{disp}}[\rho](\{R_{IJ}\})$$

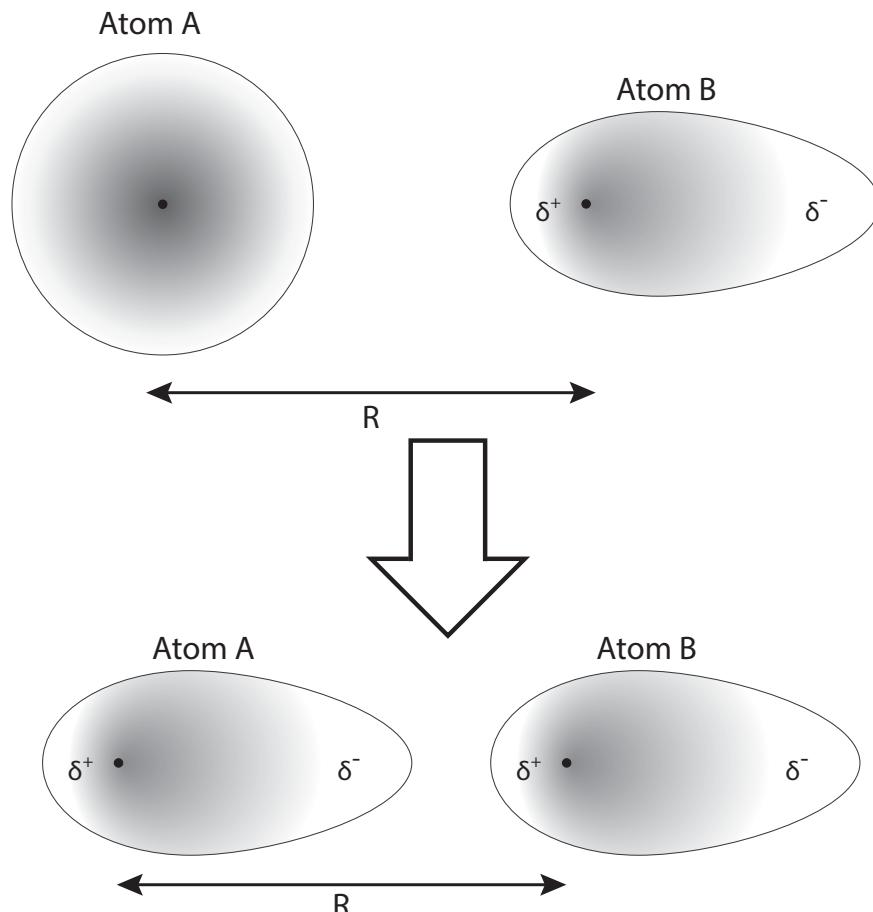
- Large amount of different functionals [4]
- Free atomic dispersion coefficients and/or (dynamic) polarizabilities
- Corrections for: molecular environment
- In solid state physics: also “van der Waals” density functionals, Vydrov-Van Voorhis
- Typically: isotropic (despite sizeable anisotropy)
- Typically: no self-consistent effect on density (relevance unclear)

4. S Grimme, A. Hansen, J.G. Brandenburg, C. Bannwarth. *Chem. Rev.* **116** (9), 5105-5154 (2016)

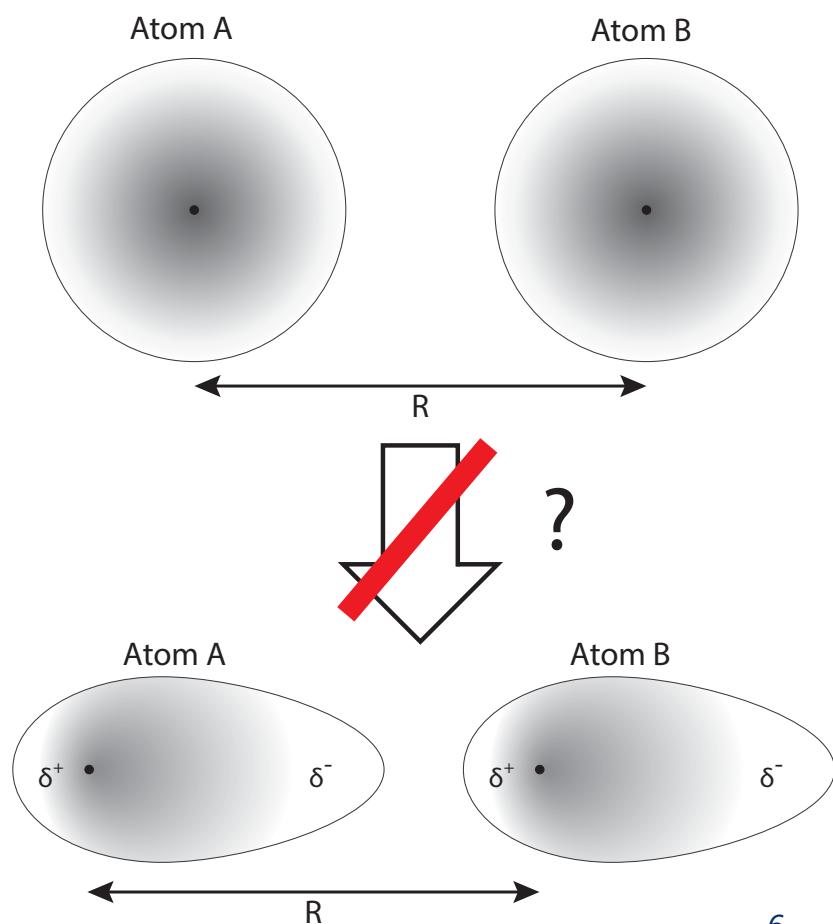
Real-space picture of induction and dispersion

$$\rho(\mathbf{r}) = N \sum_{\sigma} \int d\mathbf{x}_{2...N} |\Psi(\mathbf{r}\sigma, \mathbf{x}_{2...N})|^2$$

Induction $B \rightarrow A$



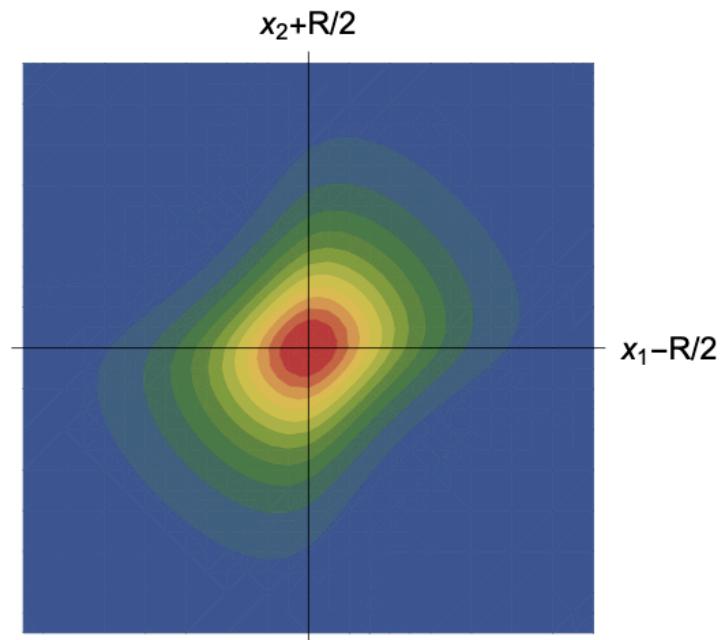
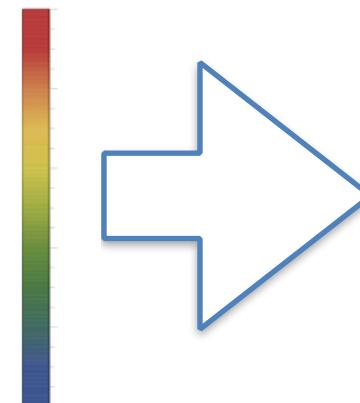
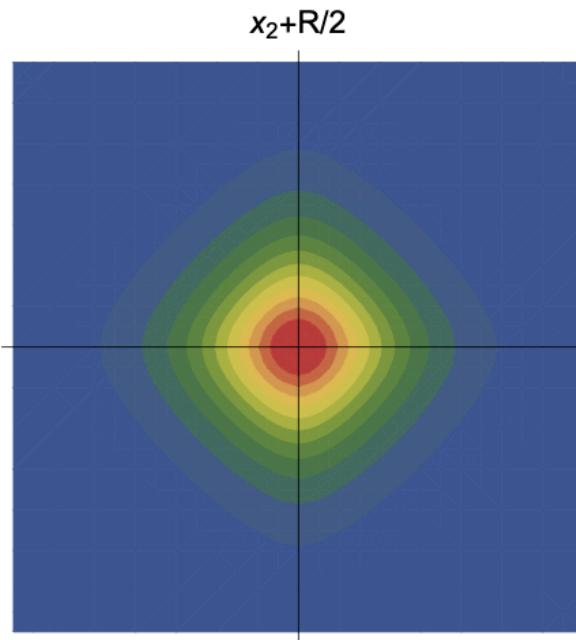
Dispersion



Real-space picture of induction and dispersion

$$P(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \sum_{\sigma_1 \sigma_2} \int d\mathbf{x}_{3\dots N} |\Psi(\mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2, \mathbf{x}_{3\dots N})|^2$$

Dispersion

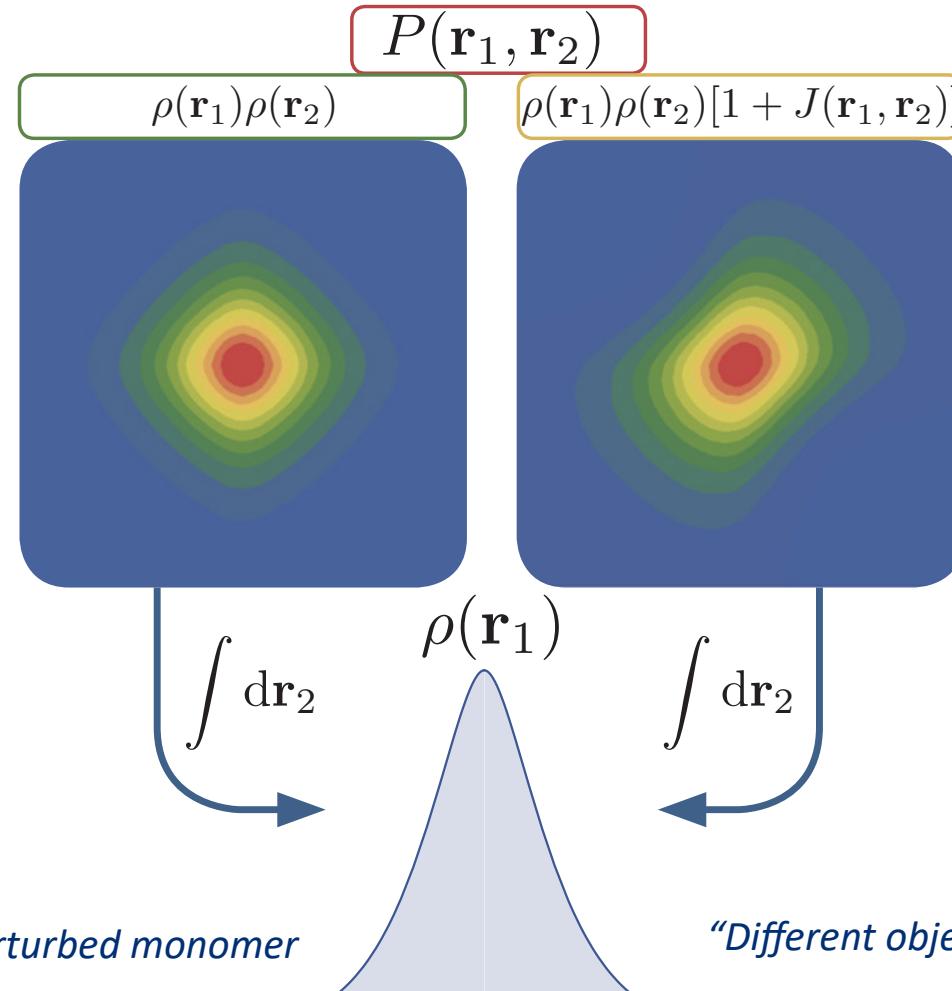


$$E_{\text{disp}}^{AB}(R) = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{P^{AB}(1)(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

7

Real-space picture of induction and dispersion

$$\rho(\mathbf{r}_1) = \frac{1}{N - 1} \int d\mathbf{r}_2 P(\mathbf{r}_1, \mathbf{r}_2)$$



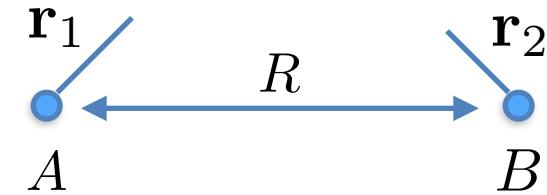
Density of unperturbed monomer

"Different object, same shadow"

Variational wave function with fixed monomer densities

Let's first treat two N=1 systems:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_0^A(\mathbf{r}_1)\phi_0^B(\mathbf{r}_2)\sqrt{1 + J(\mathbf{r}_1, \mathbf{r}_2)}$$



e.g., for two H atoms $\phi_0^A(r) = \frac{e^{-r}}{\sqrt{\pi}}$

- The density constraint is given as:

$$\int d\mathbf{r}_2 |\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\phi_0^A(\mathbf{r}_1)|^2 = \rho^A(\mathbf{r}_1)$$

And similar for B.

- This leads one to:

$$\int d\mathbf{r}_2 \rho^B(\mathbf{r}_2) J(\mathbf{r}_1, \mathbf{r}_2) = \int d\mathbf{r}_1 \rho^A(\mathbf{r}_1) J(\mathbf{r}_1, \mathbf{r}_2) = 0$$

Caveat: $J(\mathbf{r}_1, \mathbf{r}_2) \geq -1$ but true for $R \rightarrow \infty$

- Expand J_R in a one-particle basis of “dispersals”

$$J(\mathbf{r}_1, \mathbf{r}_2) = \sum_{ij} c_{ij} b_i^A(\mathbf{r}_1) b_j^B(\mathbf{r}_2)$$

variational parameters

$$b_i^A(\mathbf{r}) = f_i^A(\mathbf{r}) - \int d\mathbf{r}' \frac{\rho^A(\mathbf{r}')}{N_A} f_i^A(\mathbf{r}')$$

basis functions (choose a priori)

- Density constraint: Gram-Schmidt orthogonalisation

$$E_{\text{disp}}(R) = \min_{\{c_{ij}\}} \langle \Psi_R | \hat{T} + \hat{H}_{\text{int}} | \Psi_R \rangle$$

$$- T_0^A - T_0^B - E_{\text{el-stat}}[\rho^A, \rho^B]$$

Variational wave function with fixed monomer densities

$$\langle \Psi_R | \hat{H}_{\text{int}} | \Psi_R \rangle - E_{\text{el-stat}}[\rho_A, \rho_B] = \\ \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_A(\mathbf{r}_1) \rho_B(\mathbf{r}_2) J(\mathbf{r}_1, \mathbf{r}_2) H_{\text{int}}(\mathbf{r}_1, \mathbf{r}_2)$$

$$\langle \Psi_R | \hat{T} | \Psi_R \rangle - T_0^A - T_0^B = \\ \frac{1}{8} \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_A(\mathbf{r}_1) \rho_B(\mathbf{r}_2) \frac{|\nabla_{\mathbf{r}_1} J(\mathbf{r}_1, \mathbf{r}_2)|^2 + |\nabla_{\mathbf{r}_2} J(\mathbf{r}_1, \mathbf{r}_2)|^2}{1 + J(\mathbf{r}_1, \mathbf{r}_2)} \\ \approx \frac{1}{8} \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_A(\mathbf{r}_1) \rho_B(\mathbf{r}_2) (|\nabla_{\mathbf{r}_1} J(\mathbf{r}_1, \mathbf{r}_2)|^2 + |\nabla_{\mathbf{r}_2} J(\mathbf{r}_1, \mathbf{r}_2)|^2)$$

- Approximations of kinetic energy corresponds to 2nd order PT

Variational wave function with fixed monomer densities

$$E_{\text{disp}}(R) = \min_{\{c_{ij}\}} \left(\sum_{ij} c_{ij} w_{ij} + \frac{1}{8} \sum_{ijkl} c_{ij} c_{kl} (\tau_{ik}^A S_{jl}^B + S_{ik}^A \tau_{jl}^B) \right)$$

$$w_{ij} = \int d\mathbf{r}_1 d\mathbf{r}_2 \rho^A(\mathbf{r}_1) \rho^B(\mathbf{r}_2) b_i(\mathbf{r}_1) b_j(\mathbf{r}_2) H_{\text{int}}(\mathbf{r}_1, \mathbf{r}_2)$$

$$\tau_{ij} = \int d\mathbf{r} \rho(\mathbf{r}) \nabla_{\mathbf{r}} b_i(\mathbf{r}) \cdot \nabla_{\mathbf{r}} b_j(\mathbf{r})$$

$$S_{ij} = \int d\mathbf{r} \rho(\mathbf{r}) b_i(\mathbf{r}) b_j(\mathbf{r})$$

- Optimise quadratic energy: linear system
- Diagonalise S : sylvester equation
- Diagonalise τ with S as metric:

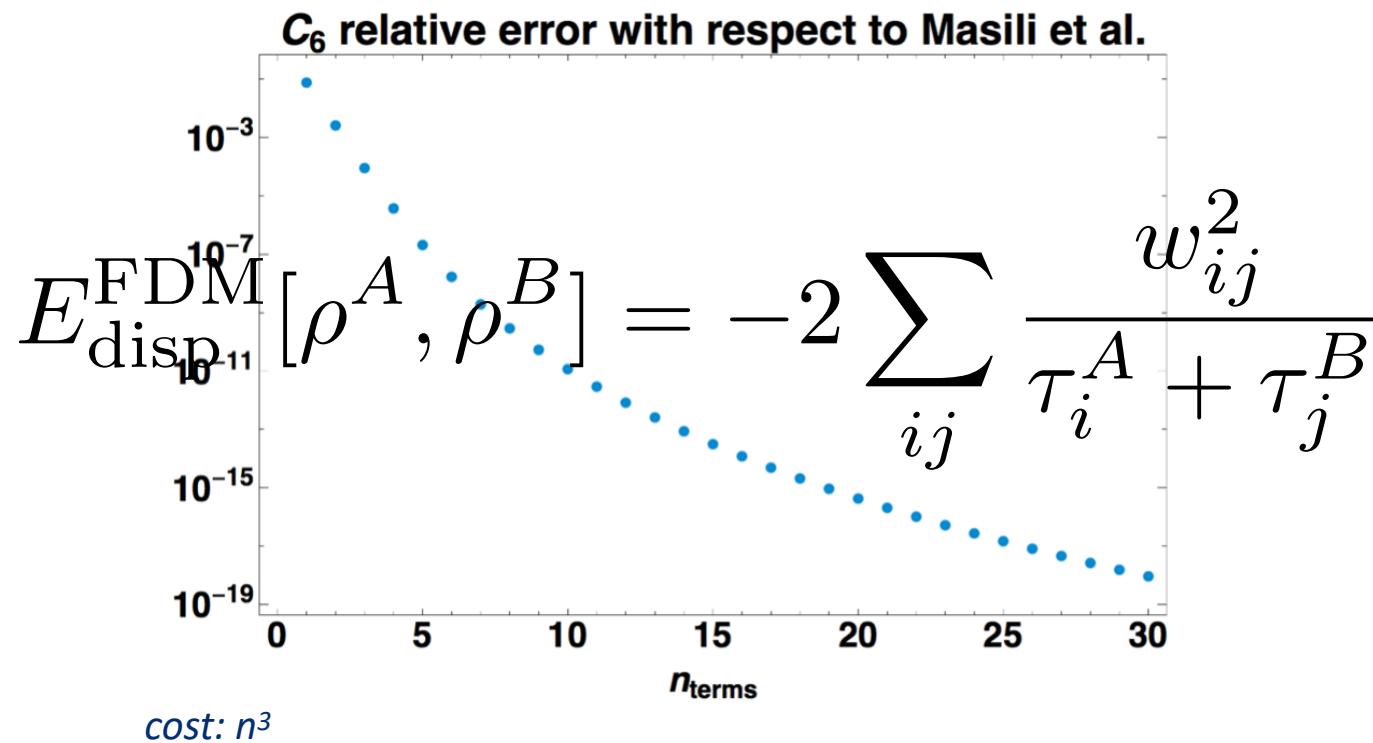
$$c_{ij} = -4 \frac{w_{ij}}{\tau_i^A + \tau_j^B}$$

Cost: $O(n_A^3 + n_B^3)$

12

Some results

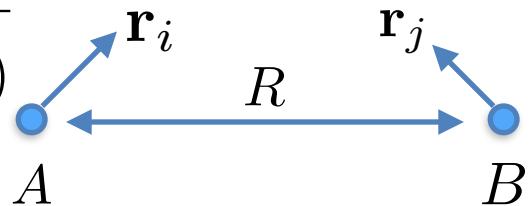
<i>H-H</i>	Thakkar ²²	Masili et al. ²³	this work (30 terms)
C_6	$6.4990267054058405 \times 10^0$	$6.4990267054058393 \times 10^0$	$6.4990267054058393 \times 10^0$
C_8	$1.2439908358362235 \times 10^2$	n.a.	$1.2439908358362234 \times 10^2$
C_{10}	$3.2858284149674217 \times 10^3$	n.a.	$3.2858284149674217 \times 10^3$



$$f_i(\mathbf{r}) = r^{n_i} Y_{l_i, m_i}(\theta, \phi)$$

1. DPK & P. Gori-Giorgi, *J. Phys. Chem. Lett.* 10, 1537 (2019)
5. M. Masili, *R.J. Gentil. Phys. Rev. A.* 78, 034701 (2008)
6. A.J. Thakkar, *J. Chem. Phys.* 89, 2092–2098 (1988)

Variational wave function with fixed monomer density

$$\Psi(\underline{\mathbf{x}}_A, \underline{\mathbf{x}}_B) = \Psi_0^A(\underline{\mathbf{x}}_A)\Psi_0^B(\underline{\mathbf{x}}_B) \sqrt{1 + \sum_{i \in A, j \in B} J(\mathbf{r}_i, \mathbf{r}_j)}$$


- The density constraint produces the same condition.
- Expand J_R in a one-particle basis of “dispersals”, etc.

$$w_{ij} = \int d\mathbf{r}_{1_A} \int d\mathbf{r}_{1_B} \left(\rho^A(\mathbf{r}_{1_A}) b_i^A(\mathbf{r}_{1_A}) + \int d\mathbf{r}_{2_A} P^A(\mathbf{r}_{1_A}, \mathbf{r}_{2_A}) b_i^A(\mathbf{r}_{2_A}) \right)$$
$$H_{\text{int}}(\mathbf{r}_{1_A}, \mathbf{r}_{1_B}) \left(\rho^B(\mathbf{r}_{1_B}) b_j^B(\mathbf{r}_{1_B}) + \int d\mathbf{r}_{2_B} P^B(\mathbf{r}_{1_B}, \mathbf{r}_{2_B}) b_j^B(\mathbf{r}_{2_B}) \right)$$

$$S_{ij} = \int d\mathbf{r} \rho(\mathbf{r}) b_i(\mathbf{r}) b_j(\mathbf{r}) + \int d\mathbf{r} d\mathbf{r}' P(\mathbf{r}, \mathbf{r}') b_i(\mathbf{r}) b_j(\mathbf{r}')$$

- Expand interaction:

 $C_n[P_2^A, P_2^B]$
*dispersion coefficients
in terms of monomer
pair densities*

“Fixed Diagonal Matrices”

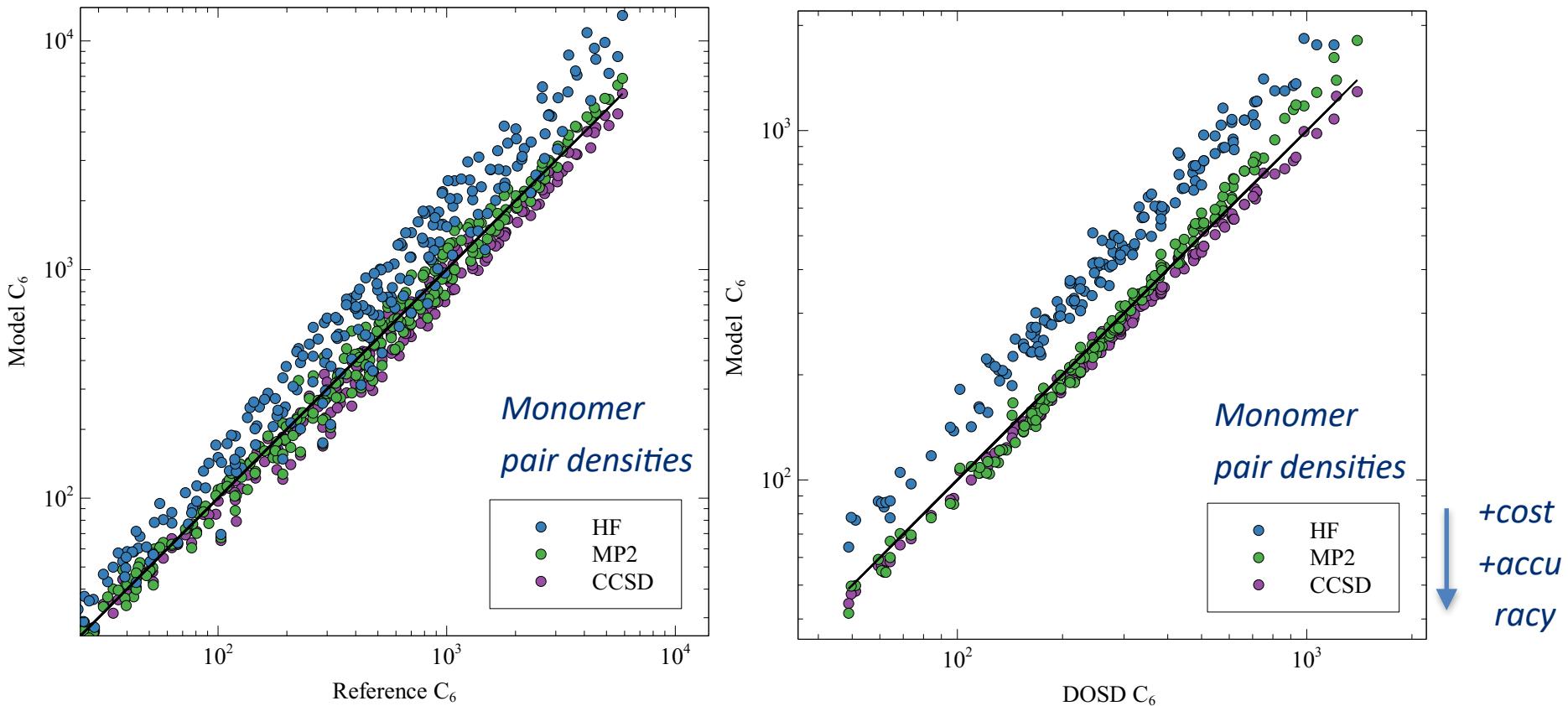
- Accidentally, the density constraint enforces fixed pair density on the monomers
- And 3-body density, 4-body density, etc...

$$E_{\text{disp}}^{\text{FDM}}(R) = \min_{\Psi_R \rightarrow \left| \Psi_0^A \right|^2, \left| \Psi_0^B \right|^2} \left\langle \Psi_R \left| \hat{T} + \hat{V}_{ee}^{\text{AB}} \right| \Psi_R \right\rangle - T_0^A - T_0^B - U[\rho^A, \rho^B]$$

- No change in electron-electron interaction on the monomer

$$f_i(\mathbf{r}) = x^{p_i} y^{q_i} z^{s_i}$$

- Left: 253 atomic pairs, right: 157 molecular pairs



- MAPE atoms: 52.3% (HF), 12.1% (MP2), 11.9% (CCSD)
- MAPE molecules: 57.1% (HF), 7.9% (MP2), 7.2% (CCSD)
- Anisotropic coefficients similar accuracy

See 3. DPK, T. Weckman & P. Gori-Giorgi, J. Chem. Theory Comput. (2021) doi: 10.1021/acs.jctc.1c00102 and references therein 16

- Functional derivative can be computed

$$\frac{\delta E_{\text{disp}}^{\text{FDM}}[\rho^A, \rho^B]}{\delta \rho^A(\mathbf{r})} = 2 \sum_{pqr} \left(\dot{\tau}_{rp}^A(\mathbf{r}) + \tau_q^B \dot{S}_{rp}^A(\mathbf{r}) \right) \frac{w_{pq} w_{rq}}{(\tau_p^A + \tau_q^B)(\tau_r^A + \tau_q^B)} \\ - 4 \sum_{pq} \frac{\dot{w}_{pq}^A(\mathbf{r}) w_{pq}}{\tau_p^A + \tau_q^B},$$

- Dotted quantities are functional derivatives of matrix elements
- Somewhat lengthy derivation in SM of [2]

Virial Theorem

In perturbation theory we don't need to satisfy the Virial theorem for the exact energy. All we need is $H_{\text{int}} : H_0, -2 : 1$.

Component (C_6)	Exact	Our work	Hylleraas VPT
H_{int}	-2	-2	-2
V_{ext}	+6	0	1.304...
$V = H_{\text{int}} + V_{\text{ext}}$	+4	-2	-0.696...
T	-5	+1	-0.304...
$T + V_{\text{ext}} = H_0$	+1	+1	+1
Total	-1	-1	-1

All give exact total energy, but shift contributions between V_{ext} and T .

For exact: see Levine Quantum Chemistry book

Approximate exchange-correlation holes: He-He

- Goal is to use approximate pair densities or exchange-correlation holes to obtain a density functional
- Weak-interacting limit (Kohn-Sham) and strong-interacting limit (Strictly Correlated Electrons [10])

He-He

Pair density	Accurate [8]	Physical [9]	KS	SCE
C6 (a.u.)	1.460978	1.458440	1.70615	0.478433
% of accurate		99.8%	116.8%	32.7%

- In general: KS exchange-hole from DFA performs worse than HF

8. Z.-C. Yan , J. F. Babb , A. Dalgarno and G. W. F. Drake , Phys. Rev. A, 1996, **54** , 2824 –2833

9. D.E. Freund, B.D. Huxtable, J.D. Morgan. Phys. Rev. A. 29, 980–982 (1984)

10. M. Seidl , P. Gori-Giorgi and A. Savin , Phys. Rev. A, 2007, **75** , 042511

- We designed a method, which yields:

$$C_{2n}[P_2^A, P_2^B]$$

- Dispersion coefficient C_6 sufficiently accurate for closed-shell systems with no density distortion
- Isotropic and anisotropic similar accuracy
- Goal, in progress:

$$C_{2n}[P_2^A, P_2^B] = C_{2n}[\rho^A, h_{\text{xc}}^A, \rho^B, h_{\text{xc}}^B] \rightarrow C_{2n}[\rho^A, \rho^B]$$

- Goal, in progress: without multipolar expansion

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1. DPK & P. Gori-Giorgi, *J. Phys. Chem. Lett.* 10 (7), 1537-1541 (2019) doi: 10.1021/acs.jpclett.9b00469

2. DPK & P. Gori-Giorgi, *Faraday Discuss.*, 224, 145-165 (2020) doi: 10.1039/D0FD00056F

3. DPK, T. Weckman & P. Gori-Giorgi, *J. Chem. Theory Comput.* (2021) doi: 10.1021/acs.jctc.1c00102

And references therein.

3a. DPK. Fixed Diagonal Matrices. <https://github.com/DerkKooi/fdm>

