

London dispersion interactions with fixed marginals

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Outline

- ▶ Introduction to dispersion
- ▶ Interaction Hamiltonian (H_2)
- ▶ Results
- ▶ Mathematical aspects of the method to explore
- ▶ Perspectives and conclusion

Introduction to dispersion

- ▶ van der Waals (two-body) forces: multipole - multipole (electrostatic), induced multipole - multipole (induction) and induced multipole - induced multipole interactions (dispersion).
- ▶ The first dispersion term between neutral atoms and molecules goes as R^{-6} , where R is the intermolecular distance.
- ▶ London^[1] showed that it results from second-order perturbation theory, still standard treatment.
- ▶ Lieb and Thirring^[2] proved its universal nature:

$$E_{A+B}(R) < E_A^0 + E_B^0 - \frac{C_6}{R^6}, \quad R \rightarrow \infty \quad (1)$$

(Note: For atoms and certain orientations of molecules)

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H₂ Hamiltonian

$$\hat{H} = \hat{H}_A + \hat{H}_B + \hat{H}_{int} \quad (2)$$

► Expand:

$$\hat{H}_{int} = \sum_{n=1}^{\infty} R^{-n} \hat{H}_{int,n} \quad (3)$$

► We find $\hat{H}_{int,1} = \hat{H}_{int,2} = 0$ (neutral systems).

$$\hat{H}_{int,3} = x_1 x_2 + y_1 y_2 - 2z_1 z_2 \quad (4)$$

Interesting note: interaction is the attractive/repulsive harmonic one. In general all terms are separable (termwise!).

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Dispersion without marginal change

Two one-particle systems:

$$\Psi_R(\mathbf{r}_1, \mathbf{r}_2) = \phi_0^A(\mathbf{r}_1)\phi_0^B(\mathbf{r}_2)\sqrt{1 + J_R(\mathbf{r}_1, \mathbf{r}_2)} \quad (5)$$

($|J_R(\mathbf{r}_1, \mathbf{r}_2)| \ll 1$) Conserve monomer marginal (fixes V_{ext}):

$$\int d\mathbf{r}_2 |\Psi_R(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\phi_0^A(\mathbf{r}_1)|^2, \quad \int d\mathbf{r}_1 |\Psi_R(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\phi_0^B(\mathbf{r}_2)|^2 \quad \forall R \quad (6)$$

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Parametrize:

$$J_R(\mathbf{r}_1, \mathbf{r}_2) = \sum_{ij} c_{ij,R} b_i^A(\mathbf{r}_1) b_j^B(\mathbf{r}_2) = \sum_{ij} c_{ij,R} (f_i^A(\mathbf{r}_1) - p_i^A) (f_j^B(\mathbf{r}_2) - p_j^B) \quad (8)$$

$$p_i = \frac{1}{N} \int d\mathbf{r} |\phi_0(\mathbf{r})|^2 f_i(\mathbf{r}) = \frac{1}{N} \int d\mathbf{r} \rho_0(\mathbf{r}) f_i(\mathbf{r}) \quad (9)$$

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Results H_2

In the end we get $C_n[\phi_0^A, \phi_0^B] \equiv C_n[\rho_0^A, \rho_0^B]$. Choose basis for f_i :

$$f_i(\mathbf{r}) = x^{s_i} y^{t_i} z^{u_i} \vee r_i^{n_i} Y_{l_i, m_i}(\theta, \phi) \quad (10)$$

Coefficient	Thakkar [3]	This work (20 terms)	This work (30 terms)
6	$6.4990267054058405 \times 10^0$	$6.4990267054058\mathbf{366} \times 10^0$	$6.4990267054058\mathbf{393} \times 10^0$
8	$1.2439908358362235 \times 10^2$	$1.24399083583622\mathbf{33} \times 10^2$	$1.24399083583622\mathbf{34} \times 10^2$
10	$3.2858284149674217 \times 10^3$	$3.28582841496742\mathbf{16} \times 10^3$	$3.2858284149674217 \times 10^3$
12	$1.2148602089686110 \times 10^5$	$1.2148602089686110 \times 10^5$	ibid.
14	$6.0607726891921249 \times 10^6$	$6.0607726891921249 \times 10^6$	ibid.
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Masili et al. [4]: 6.4990267054058**393**131281946041

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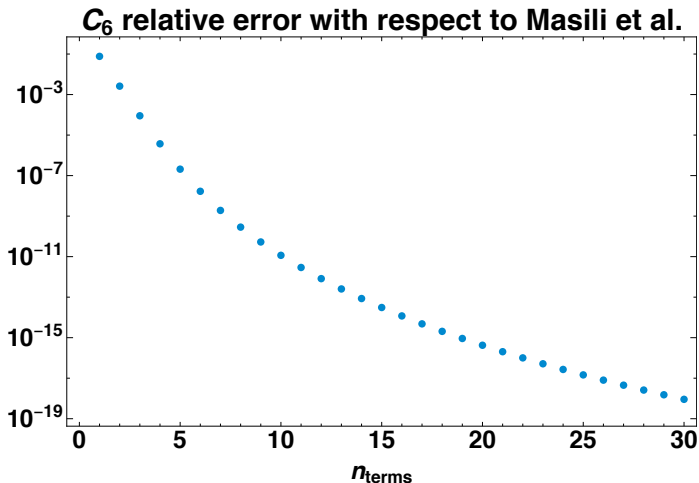
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Convergence with respect to Masili et al. [4] Scaling: $\mathcal{O}(n_{\text{terms}}^3)$.

Dispersion without density change

Ansatz for N_A and N_B electron system

$$\Psi_R(\underline{\mathbf{x}}_A, \underline{\mathbf{x}}_B) = \Psi_0^A(\underline{\mathbf{x}}_A) \Psi_0^B(\underline{\mathbf{x}}_B) \sqrt{1 + \sum_{i \in A, j \in B} J(\mathbf{r}_i, \mathbf{r}_j)} \quad (11)$$

Fix the N_A and N_B -body marginals on both systems (fixing $V_{ee}^A + V_{ee}^B$):

$$\int d\underline{\mathbf{x}}_B |\Psi_R(\underline{\mathbf{x}}_A, \underline{\mathbf{x}}_B)|^2 = |\Psi_A(\underline{\mathbf{x}}_A)|^2 \quad \forall \underline{\mathbf{x}}_A, A \leftrightarrow B \quad (12)$$

Also generated by,

$$\int d\mathbf{r}_{1A} \rho_A(\mathbf{r}_{1A}) J(\mathbf{r}_{1A}, \mathbf{r}_{1B}) = 0 \quad \forall \mathbf{r}_{1B}, A \leftrightarrow B \quad (13)$$

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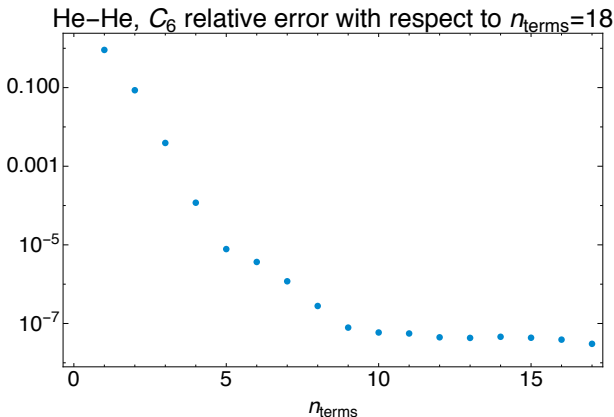
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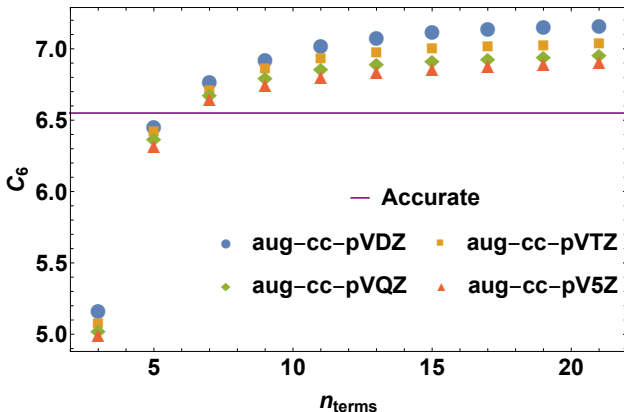
Dispersion without density change

$C_6[P_2^A, P_2^B]$ for He-He (0.17% error):



P_2 from wf of Freund, Huxtable and Morgan.^[5] Accurate: Yan^[6]

Dispersion without density change

 $C_6[P_2^A, P_2^B]$ for Ne-Ne (5.5% error): P_2 from Hartree-Fock. Accurate: Thakkar, et al. [7]

Mathematical aspects

- ▶ What are the properties of the function space in which the b_i (or f_i) live?
- ▶ We need to demand:

$$S_{ij} = \int \rho(\mathbf{r}) b_i(\mathbf{r}) b_j(\mathbf{r}) d\mathbf{r} < \infty \quad (14)$$

- ▶ $b_i \in$ weighted L^2 space with ρ as weighting factor?

$$\tau_{ij} = \int \rho(\mathbf{r}) \nabla_{\mathbf{r}} b_i(\mathbf{r}) \cdot \nabla_{\mathbf{r}} b_j(\mathbf{r}) d\mathbf{r} < \infty \quad (15)$$

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- ▶ We need to demand:

$$S_{ij} = \int \rho(\mathbf{r}) b_i(\mathbf{r}) b_j(\mathbf{r}) d\mathbf{r} < \infty \quad (14)$$

- ▶ $b_i \in$ weighted L^2 space with ρ as weighting factor?

$$\tau_{ij} = \int \rho(\mathbf{r}) \nabla_{\mathbf{r}} b_i(\mathbf{r}) \cdot \nabla_{\mathbf{r}} b_j(\mathbf{r}) d\mathbf{r} < \infty \quad (15)$$

- ▶ $b_i \in$ weighted H^1 space?
- ▶ Which space? Convergence within this space? What constitutes a complete set of $b_i(\mathbf{r})$? Polynomials complete?
- ▶ Does this ensure all other integrals are also finite?

Conclusion and Perspective

- ▶ Novel method to treat dispersion (multipole expansion not needed)
- ▶ Requires only ground-state properties, bottleneck: pair density (2-RDM) integrals, method scales as $\mathcal{O}(n_{\text{terms}}^{A3} + n_{\text{terms}}^{B3})$
- ▶ Very accurate for atoms, molecules ongoing (and lack reference data)
- ▶ Approximations for the ground-state wf to be tried (up to now HF)
- ▶ DFT: $C_6[P_2^A, P_2^B] = C_6[\rho^A, h_{\text{xc}}^A, \rho^B, h_{\text{xc}}^B] \rightarrow C_6[\rho^A, \rho^B]$

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Thank you for your attention! Questions?

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