Dispersion without many-body density distortion: Assessment on atoms and small molecules

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Abstract

We have implemented and tested the method we have recently proposed [J. Phys. Chem. Lett. 10, 1537 (2019)] to treat dispersion interactions derived from a supramolecular wavefunction constrained to leave the diagonal of the many-body reduced density matrix of each monomer unchanged. The corresponding variational optimization leads to expressions for the dispersion coefficients in terms of the ground-state pair densities of the isolated monomers only. We have used three levels of theory for the ground-state monomer pair densities: Hartree-Fock, MP2 and CCSD, looking at both isotropic and anisotropic dispersion coefficients. For closed-shell systems, CCSD monomer pair densities yield the best results with smaller variance, with mean average percent error on isotropic dispersion coefficients of about 7%, and similar accuracy for anisotropies. The performance for open shell systems is less satisfactory, with CCSD not always providing the best result.
1 Introduction

The attractive London dispersion interaction between atoms and molecules is weaker than covalent bonding forces, but while the latter decay exponentially with the separation $R$ between the monomers, dispersion interactions decay only polynomially in $1/R$. Because of this dominating long range character, dispersion plays a crucial role in various chemical systems and processes, such as protein folding, soft solid state physics, gas–solid interfaces etc. An accurate, computationally efficient, and fully nonempirical treatment of dispersion forces remains an open challenge, and it is the objective of several ongoing efforts (see, e.g., refs \[1\] and \[2\] for recent reviews and benchmarks).

We have recently introduced a class of variational wave functions that capture the long-range interactions between two quantum systems without deforming the diagonal of the many-body density matrix of each monomer.\[4\] This way, dispersion is reduced to a balance between kinetic energy and monomer-monomer interactions only, providing an explicit expression for the dispersion coefficients in terms of the ground-state pair densities of the isolated monomers. Although the supramolecular wavefunction constructed in this way can never be exact, as density distortion is prohibited, it provides a variational expression for the dispersion coefficients when accurate pair densities for the monomers are used, at a computational cost given essentially by the ground-state monomer calculations. The method has been found to yield exact results for the dispersion coefficients up to $C_{10}$ for the H-H case, and very accurate results (0.17% error on $C_{6}$) for He-He and He-H.\[4\] This is also conceptually interesting, as it shows that, although in the exact case we know that the monomer densities must be distorted\[5-8\] to yield the force at order $R^{-7}$, very accurate or even exact dispersion coefficients can be obtained by explicitly freezing the monomer densities at their isolated ground-state shape. Moreover, the expressions for the dispersion coefficients in terms of the ground-state pair densities of the isolated monomers offer a neat theoretical framework to build new approximations, by using pair densities from different levels of accuracy, including exchange-correlation hole approximations from density functional theory.
The aim of this work is to explore the performance of the method for the dispersion $C_6$ coefficient for atoms and small molecules using different levels of theory for the monomer calculations, studying the convergence and basis set dependence of the results. We test the approach on 459 pairs of atoms, ions, and small molecules, using Hartree-Fock (HF), second-order Møller-Plesset perturbation theory (MP2) and coupled cluster with singles and doubles (CCSD) ground-state pair densities. We should keep in mind that the method is guaranteed to be variational, yielding a lower bound to $C_6$, only when we use exact pair densities of the monomers. As we shall see, for closed shell systems, this is almost always the case with CCSD pair densities, which yield in general rather accurate results (of the same quality of linear-response CCSD, but at the cost of a ground state calculation), slightly underestimating $C_6$, although there are exceptions. With HF pair densities, as it was already found in a preliminary result for the Ne-Ne case in Ref. 4, $C_6$ is, in the vast majority of cases, overestimated.

2 Theory

We consider two systems $A$ and $B$ separated by a (large) distance $R$. Instead of performing Rayleigh-Schrödinger perturbation theory, we use the wavefunction ansatz of ref [4]

$$
\Psi(x_A, x_B) = \Psi^A_0(x_A)\Psi^B_0(x_B) \sqrt{1 + \sum_{i\in A, j\in B} J_R(r_i, r_j)},
$$

where $x$ denotes the spin-spatial coordinates $(r, \sigma)$ and $x_{A/B}$ denote the whole set of the spin-spatial coordinates of electrons in system $A/B$. $\Psi^A_0$ and $\Psi^B_0$ are the isolated ground-state wavefunctions of systems $A$ and $B$. The function $J_R$ correlates electrons in $A$ with those in $B$, and is written in the form,

$$
J_R(r, r') = \sum_{ij} c_{ij,R}b^A_i(r)b^B_j(r'),
$$
where \( c_{ij,R} \) are parameters, which are determined variationally. The functions \( b_{i}^{A/B}(r) \) for now are an arbitrary set of “dispersal” functions, used as basis to expand \( J_{R} \). The constraint that the diagonal of the many-body density matrix of each fragment stays unchanged is enforced by imposing:

\[
\int \rho_{0}^{A}(r_{iA})J_{R}(r_{iA}, r_{jB})dr_{iA} = 0 \quad \forall \, r_{jB} \tag{3}
\]

\[
\int \rho_{0}^{B}(r_{jB})J_{R}(r_{iA}, r_{jB})dr_{jB} = 0 \quad \forall \, r_{iA}, \tag{4}
\]

with \( \rho_{0}^{A(B)} \) the ground-state one-electron densities of the two systems. Thanks to this constraint, the expectation of the external potential and of the electron-electron interactions inside each monomer cancel out in the interaction energy, whose variational minimization takes a simplified form. When performing the usual multipolar expansion of the monomer-monomer interaction, we can, accordingly, expand \( c_{ij,R} \) in a series of inverse powers of \( R \),

\[
c_{ij,R} = c_{ij}^{(3)}R^{-3} + c_{ij}^{(4)}R^{-4} + c_{ij}^{(5)}R^{-5} + \mathcal{O}(R^{-6}), \tag{5}
\]

which leads to explicit expressions for the dispersion coefficients. In this paper, we focus on the leading \( C_{6} \) coefficient of the term \(-C_{6}R^{-6}\) in the dispersion interaction energy, which is determined by the variational parameters \( c_{ij}^{(3)} \) in eq (5), denoted simply \( c_{ij} \) in the rest of this work.

As detailed in the supplementary material of ref 4, the variational equation for \( C_{6} \) corresponding to our wave function is given in terms of the matrices \( \tau_{ij}^{A/B} \), \( S_{ij}^{A/B} \), and \( P_{ij}^{A/B} \) (which determine the kinetic correlation energy),

\[
S_{ij}^{A} = \int \rho_{0}^{A}(r)b_{i}^{A}(r)b_{j}^{A}(r) \, dr, \tag{6}
\]

\[
\tau_{ij}^{A} = \int \rho_{0}^{A}(r)\nabla b_{i}^{A}(r) \cdot \nabla b_{j}^{A}(r) \, dr, \tag{7}
\]

\[
P_{ij}^{A} = \int dr_{1A} \int dr_{2A} P_{0}^{A}(r_{1A}, r_{2A})b_{i}^{A}(r_{1A})b_{j}^{A}(r_{2A}), \tag{8}
\]
with similar expressions for system $B$, and of the matrix $w_{ij}$ (which determines the monomer-
monomer interaction),

$$w_{ij} = \sum_{e=x,y,z} h_e (d_{e,i}^A + D_{e,i}^A)(d_{e,j}^B + D_{e,j}^B),$$  \hspace{1cm} (9)

with $e = x, y, z$, and $h_e = (1, 1, -2)$ when the intermolecular axis is parallel to the $z$-axis. The vectors $d_i^A$ and $D_i^A$ determine the dipole–dipole interaction terms,

$$d_i^A = \int dr_1 A \rho_0^A(r_1 A) b_i^A(r_1 A) r_1 A$$
$$D_i^A = \int dr_1 A \int dr_2 A P_0^A(r_1 A, r_2 A) b_i^A(r_2 A) r_1 A,$$  \hspace{1cm} (10)

with, again, similar expressions for monomer $B$. In eqs (8) and (11) $P_{0}^{A/B}$ is the ground-state pair density of the two monomers, with usual normalization to $N(N - 1)$.

In our previous work\textsuperscript{4} the matrices $S_{ij}^{A/B} + P_{ij}^{A/B}$ were diagonalized through a Löwdin orthogonalization among the $b_i$’s, transforming the matrices $w_{ij}$ and $\tau_{ij}^{A/B}$ accordingly. The variational coefficients $c_{ij}$ were then determined via the solution of a Sylvester equation,\textsuperscript{4,9}

$$\sum_k \tau_{ik}^A c_{kj} + \sum_l c_{il} \tau_{lj}^B = -4 w_{ij}.$$  \hspace{1cm} (12)

Here we diagonalize $\tau_{ij}^{A/B}$ with $S_{ij}^{A/B} + P_{ij}^{A/B}$ as a metric through a generalized eigenvalue problem, again transforming accordingly $w_{ij}$, so that the indices indicate from now on matrix elements with the transformed $b_i$’s. The advantage is that this eigenvalue problem needs to be solved only once for each monomer, while the Sylvester equation (12) needs to be solved
for each pair $AB$. This way we can directly obtain the variational coefficients $c_{ij}$ as

$$
\sum_k \delta_{ik} \tau_i^A c_{kj} + \sum_l \delta_{jl} \tau_j^B c_{il} = 4 w_{ij},
$$

(13)

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

(14)

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

(15)

The dispersion coefficient $C_6$ then takes the simpler (and computationally faster) form

$$
C_6^{AB} = - \sum_{ij} c_{ij} w_{ij} - \frac{1}{8} \sum_{ij} c_{ij}^2 (\tau_i^A + \tau_j^B) = \sum_{ij} \frac{2 w_{ij}^2}{\tau_i^A + \tau_j^B}.
$$

(16)

For molecules, eq (16) gives access to the orientation-dependent $C_6^{AB}$ coefficient, where the kinetic energy terms $\tau_i^{A/B}$ are clearly rotationally invariant, and the dependence on the relative orientation of the monomers enters through $w_{ij}$, as shown by eqs (9)-(11). In order to compare with values from the literature, it is often necessary to compute the orientation-averaged isotropic $C_6^{AB}$ coefficients, which can be obtained by performing the orientation average directly on each $w_{ij}^2$, yielding

$$
\overline{C}_6^{AB} = \sum_{ij} \frac{2 \overline{w}_{ij}^2}{\tau_i^A + \tau_j^B}.
$$

(17)

The $\overline{w}_{ij}^2$ is the spherically-averaged interaction term given by

$$
\overline{w}_{ij}^2 = \frac{2}{3} \sum_{e=x,y,z} (d_{e,i}^A + D_{e,i}^A)^2 \sum_{f=x,y,z} (d_{f,j}^B + D_{f,j}^B)^2.
$$

(18)

For the case of two linear molecules one usually define anisotropies by writing the dis-
persion coefficient $C_6$ as,

$$C_6^{AB}(\theta_A, \phi_A, \theta_B, \phi_B) = C_6^{AB} \left( 1 + \Gamma_6^{AB} P_2(\cos(\theta_A)) + \Gamma_6^{BA} P_2(\cos(\theta_B)) \right) + \Delta_6^{AB} \frac{4\pi}{5} \sum_{m=-2}^{2} (3 - |m|) Y^m_2(\theta_A, \phi_A) Y^{-m}_2(\theta_B, \phi_B),$$

(19)

where $P_n$ denotes Legendre polynomials and $Y^m_\ell$ spherical harmonics. The anisotropies $\Gamma_6^{AB}$ and $\Delta_6^{AB}$ can be obtained from our formalism as,

$$\Gamma_6^{AB} = \frac{2}{3C_6} \sum_{ij} \frac{-\sum_{e=x,y,z} h_e (d_{e,i}^A + D_{e,i}^A)^2 \sum_{f=x,y,z} (d_{f,j}^B + D_{f,j}^B)^2}{\tau_i + \tau_j},$$

(20)

$$\Delta_6^{AB} = \frac{1}{3C_6} \sum_{ij} \frac{\sum_{e=x,y,z} h_e (d_{e,i}^A + D_{e,i}^A)^2 \sum_{f=x,y,z} h_f (d_{f,j}^B + D_{f,j}^B)^2}{\tau_i + \tau_j}.$$

(21)

A similar expression holds for $\Gamma_6^{BA}$, but with the roles of $A$ and $B$ exchanged.

On top of the monomer calculations, the diagonalization to compute $C_6$ scales formally as $n_A^3 + n_B^3$, where $n_{A/B}$ is the number of functions $b_{i}^{A/B}$ needed to converge, which, however, seems so far independent of system size. We should however also mention the cost of computing the matrix elements: the most computationally expensive part is the first step of the two-step contraction to obtain $P_{ij}$, which scales as $O(N_{\text{orb}}^4 n_{A/B})$, while the second step scales as $O(N_{\text{orb}}^2 n_{A/B}^2)$, as expensive as obtaining $S_{ij}$ and $\tau_{ij}$, where $N_{\text{orb}}$ is the number of spatial orbitals used in the monomer calculations.

### 3 Computational Details

#### 3.1 Choice of the dispersal functions $b_i(r)$

For the dispersal functions $b_{i}^{A/B}(r)$ of eq [2], we have chosen multipoles centered in $r_0 = (x_0, y_0, z_0)$,

$$b_i(r) = (x - x_0)^{a_i}(y - y_0)^{t_i}(z - z_0)^{u_i}.$$  

(22)
For atoms the obvious choice for \( r_0 \) is the position of the nucleus; for molecules, in this first exploration, we have set \( r_0 \) at the barycenter of nuclear charge. We include all \( b_i \), such that \( s_i + t_i + u_i \leq n_{\text{max}} \), where \( n_{\text{max}}^{A/B} \) is a parameter, which is set equal to 22 in all our calculations, which yields in general reasonably converged results (see sec 3.5 for a more detailed discussion on convergence). We should remark that the choice of eq (22) is dictated mainly by the immediate availability of integrals with one- and two-electron reduced density matrices: our goal here is to investigate whether the method is worth or not investing in further implementation and optimization. The question on how to determine the best possible \( b_i^{A/B}(r) \) is open, and we will address it in future work.

### 3.2 Matrix elements

We denote the spatial orbitals used in the monomer calculations by \( \phi_a(r) \) with indices \( a, b, c, d \). The spin-summed one-body reduced density matrix (1-RDM) is written as \( \gamma_{ab} \),

\[
\gamma(r, r') = \sum_{ab} \gamma_{ab} \phi_a(r) \phi_b(r'),
\]

normalized here to \( N \). The method only depends on the spatial diagonal \( \rho_0(r) = \gamma(r, r) \). The 2-RDM is written as \( \Gamma_{ab,cd} \), again spin-summed, corresponding to

\[
\Gamma(r_1, r_2; r'_1, r'_2) = \sum_{abcd} \Gamma_{ab,cd} \phi_a(r_1) \phi_b(r_1') \phi_c(r_2) \phi_d(r_2'),
\]

with normalization \( N(N-1) \). The method only depends on the spatial diagonal (pair density), \( P_0(r_1, r_2) = \Gamma(r_1, r_2; r_1, r_2) \).

To compute the matrix elements of sec 2 we need the 1-RDM and 2-RDM of the monomers and the integrals of the functions \( b_i(r) \) with the spatial orbitals, which, with the choice of
eq (22), are all of the kind

\[ I_{stu}^{ab} = \int (x - x_0)^s(y - y_0)^t(z - z_0)^u \phi_a(r)\phi_b(r)dr \]  

(25)

For every monomer we need to calculate \( S_{ij} \) of eq (6), \( \tau_{ij} \) of eq (7) and \( d_i \) of eq (10) from the 1-RDM, and \( P_{ij} \) of eq (8) and \( D_i \) of eq (11) from the 2-RDM. We first write all the matrix elements by assuming that the constraint of eqs (3)-(4) is satisfied, which amounts to assuming

\[ p_i = \frac{1}{N} \int b_i(r)\rho(r)dr = \sum_{ab} \frac{\gamma_{ab}}{N} I_{s_i, t_i, u_i}^{ab} = 0. \]  

(26)

When this does not hold, we make the appropriate modifications in terms of \( p_i \), see eqs (33)-(36) below.

We then have for the matrix \( S_{ij} \) of eq (6)

\[ S_{ij} = \sum_{ab} \gamma_{ab} I_{s_i+s_j, t_i+t_j, u_i+u_j}^{ab}, \]  

(27)

and for \( \tau_{ij} \) of eq (7)

\[ \tau_{ij} = s_i s_j \sum_{ab} \gamma_{ab} F_{s_i+s_j, t_i+t_j, u_i+u_j}^{ab} + t_i t_j \sum_{ab} \gamma_{ab} F_{s_i+s_j, t_i+t_j-2, u_i+u_j}^{ab} + u_i u_j \sum_{ab} \gamma_{ab} F_{s_i+s_j, t_i+t_j, u_i+u_j-2}^{ab} \]  

(28)

The components of the vector \( d_i \) of eq (10) are given by the dipole moment in directions \( e = x, y, z \). For example for the \( x \)-direction:

\[ d_{x,i} = \sum_{ab} \gamma_{ab} F_{s_i+1, t_i, u_i}^{ab}, \]  

(29)

while for \( y \) and \( z \) we get analogous expressions with \( F_{s_i, t_i+1, u_i}^{ab} \) and \( F_{s_i, t_i, u_i+1}^{ab} \), respectively. For
convenience, we also define (with analogous expressions for the y and z directions),

\[ d_{x,0} = \int (x - x_0) \rho(r) dr = \sum_{ab} \gamma_{ab} I_{1,0,0}^{ab}. \]  

(30)

The matrix \( P_{ij} \) of eq (8), which is a sort of overlap mediated by the pair density, is given by

\[ P_{ij} = \sum_{abcd} \Gamma_{ab,cd} I_{s_i,t_i,u_i}^{ab} I_{s_j,t_j,u_j}^{cd}. \]  

(31)

For the components of the vector \( D_i \) of eq (11) we have, for example in the \( x \) direction,

\[ D_{x,i} = \sum_{abcd} \Gamma_{ab,cd} I_{1,0,0}^{ab} I_{s_i,t_i,u_i}^{cd}, \]  

(32)

with similar expressions with \( I_{0,1,0}^{ab} \) and \( I_{0,0,1}^{ab} \) for the other two components. When \( p_i \) of eq (26) is not zero we need to modify the matrix elements according to

\[ S_{ij} = \sum_{ab} \gamma_{ab} I_{s_i+s_j,t_i+t_j,u_i+u_j}^{ab} - N p_i p_j \]  

(33)

\[ d_{x,i} = \sum_{ab} \gamma_{ab} I_{s_i+1,t_i,u_i}^{ab} - p_i d_{x,0} \]  

(34)

\[ P_{ij} = \sum_{abcd} \Gamma_{ab,cd} I_{s_i,t_i,u_i}^{ab} I_{s_j,t_j,u_j}^{cd} - p_i p_j N (N - 1) \]  

(35)

\[ D_{x,i} = \sum_{abcd} \Gamma_{ab,cd} I_{1,0,0}^{ab} I_{s_i,t_i,u_i}^{cd} - (N - 1) p_i d_{x,0}, \]  

(36)

with analogous expressions for the components \( y \) and \( z \) of \( d_i \) and \( D_i \), and \( d_{x,0} \) defined in eq (30).

### 3.3 Implementation

The expression for the dispersion coefficients of eqs (16) and (17), with the computational details just described, has been written in Python and interfaced with PySCF\textsuperscript{11} and Horton3.\textsuperscript{12} The reduced density matrices of the monomers are obtained from PySCF and the
multipole moment integrals are calculated using Horton3. The monomer densities and pair densities have been computed at three different levels of theory: Hartree-Fock, MP2 and CCSD. The geometries of the molecules were optimised using the ORCA program package using MP2 level of theory with def2-TZVPPD basis set.

### 3.4 Choice of the basis set for the monomer calculations

We have extensively explored the dependence on the basis set used for the monomer pair densities calculations for all but the largest molecules, finding that, in general, going beyond a def2-TZVPP (or equivalent) quality does not particularly improve the overall results, with few singular exceptions. The mean absolute errors (MAPE) for dispersion coefficients of molecules obtained with def2-QZVPP basis set differs from the def2-TZVPP ones from 1.5 to 2.2%, with Hartree–Fock being the least and CCSD the most sensitive. When diffuse functions are incorporated into the basis set, the MAPE difference between def2-TZVPP and def2-TZVPPD basis sets range from 2.6 to 3.5%, with Hartree–Fock being the least sensitive and MP2 the most sensitive. These differences are less than half the MAPE with respect to the reference values. As a representative example, in fig 1 we show the $C_{6}^{AA}$ for the molecules considered here with HF, MP2 and CCSD pair densities using different basis sets compared with calculations done using the def2-TZVPP basis set, which is our choice for all the results presented in the next section.

We should also remark that, since Hartree-Fock pair densities usually lead to an overestimation of $C_{6}$, if one uses a smaller double-ζ basis set the performance in this case usually improves as the smaller basis makes the overestimation less profound. The results obtained using a correlated pair density, however, become worse if we go below triple-ζ quality.

All our results obtained with different basis sets are available in the supplementary material.
Figure 1: Isotropic $C_6^{AA}$ dispersion coefficients for molecules calculated using Hartree–Fock, MP2 and CCSD pair densities with different basis sets compared with calculations done using def2-TZVPP basis set. Coefficients calculated with the MP2 pair density are the most sensitive to the basis set used, while Hartree–Fock and CCSD methods produce quite robust results. The largest outlier for all the methods used is the CS$_2$ molecule, which is further discussed in section 3.5 and in fig 2.

3.5 Convergence with respect to the number $n_{\text{max}}$ of $b_i$ functions

In all our calculations we have fixed $n_{\text{max}} = 22$, which yields in general well converged results for the vast majority of cases, and it is also a value for which the multipole integrals are numerically stable. However, we should remark that there are a few cases in which the convergence with the number of $b_i$ functions has not been satisfactorily reached. As a typical example for how the vast majority of systems behave, we show in the left panel of fig 2 the convergence of $C_6^{AA}$ for CH$_4$ with respect to $n_{\text{max}}$, for both HF and CCSD pair densities, with and without diffuse functions in the basis set for the monomer calculation. We see that the result is well converged and that the addition of diffuse functions has little effect, with CCSD underestimating the $C_6$ coefficient. There are however three molecules (SO$_2$, CS$_2$ and CO$_2$) where the values between $n_{\text{max}} = 20$ and $n_{\text{max}} = 22$ deviate more than 1%. The worst case is CS$_2$, shown in the right panel of the same fig 2, we see that even at $n_{\text{max}} = 28$ the dispersion coefficient of CS$_2$ is not converged and that CCSD overestimates $C_6$. The inclusion of diffuse functions, in this case, improves both the convergence profile and the accuracy.
4 Results

Dispersion coefficients were computed for four data sets:

1. $C_6^{AA}$ for 23 atoms and ions,
2. $C_6^{AB}$ for 253 mixed pairs consisting of atoms and ions,
3. isotropic $C_6^{AA}$ for a set of 26 molecules,
4. isotropic $C_6^{AB}$ for a set of 157 mixed molecule pairs,
5. anisotropic $\Gamma_6^{AB}$ and $\Delta_6^{AB}$ (where applicable) for three diatomics and interacting with noble-gas atoms.

In all cases we compare our results with reference values obtained from dipole oscillator strength distribution (DOSD) data computed or measured.
4.1 Dispersion coefficients for atoms and ions

The results for set 1, using HF, MP2 and CCSD pair densities (def2-TZVPP basis set, with effective core potential (ECP) for fifth and sixth row elements) for the monomers are presented in table 1 and compared with accurate reference data. The MAPE for Hartree-Fock, MP2 and CCSD monomer pair densities is 62.1%, 17.7% and 16.2%, respectively. The same results are also illustrated in fig 3. Notice that the result for H in table 1 has a small residual error of 1.2% due to the basis set used, since the results for $C^{AA}_6$ (as well as $C^{AA}_8$ and $C^{AA}_{10}$) from our wavefunction are exact when the exact hydrogenic orbital is used.

For the test set 2, the different pairs are formed by selecting A and B from the species listed in table 1. The results for the dispersion coefficients $C^{AB}_6$ computed using different pair densities for the monomers, again with the def2-TZVPP basis set, are compared to accurate reference values in fig 4. The MAPE for Hartree–Fock, MP2 and CCSD are slightly better, being 52.3%, 12.1%, 11.9%, respectively. All the values obtained are available in the supplementary material.

These results for atoms and ions are not extremely promising, in particular because they do not always improve with the accuracy of the theory used to treat the monomers. From fig 4, it is evident that the use of the Hartree-Fock pair densities leads to an overestimation of the dispersion coefficients. However, for some systems (Li, Na, Be+, Mg+) our method combined with correlated pair densities considerably underestimates the dispersion coefficient, and in those cases Hartree–Fock pair densities yield better results than MP2 and CCSD ones. As it should, the CCSD pair density tends to produce a lower bound for the dispersion coefficient, but with some exceptions (e.g. Ag, Cu, Ba+).

The picture improves considerably if we look at closed-shell species only: if we consider the 15 noble-gas pairs, the MAPE for HF, MP2 and CCSD pair densities is 41.9%, 12.2% and 4.3%, respectively. Also, if we consider the subset of our dataset formed by the 45 pairs of the noble gas and alkali elements used by Becke and Johnson in their original paper on the exchange-hole dipole moment (XDM) dispersion model (see their table I), we obtain
MAPE for MP2 and CCSD equal to 9.6% and 7.7%, respectively, lower than the one of XDM (11.4%), while with Hartree-Fock pair densities our MAPE is 27.3%.

Overall, these first results indicate that our variational ansatz works really well for closed-shell species, while being less reliable for open shell cases. As we shall see in the next section, the results for the isotropic dispersion coefficients for closed-shell molecules are accurate and robust, confirming these first findings.

Table 1: Dispersion coefficients $C_6^{AA}$ for a set of atoms and ions computed using Hartree–Fock, MP2 and CCSD pair densities for the monomers with the def2-TZVPP basis set, with ECP for fifth and sixth row elements. For each species, the dispersion coefficient closest to the reference value is in bold font. The mean absolute percentage error (MAPE) as well as the maximum absolute percent deviation (AMAX) for the data set are reported.

| Species | Ref. [14] | HF   | MP2  | CCSD  |
|---------|-----------|------|------|-------|
| H       | 6.50      | 6.42 | 6.42 | 6.42  |
| Li      | 1395.80   | 1024.59 | 1013.58 | 981.77 |
| Na      | 1561.60   | 1458.17 | 1400.47 | 1211.02 |
| K       | 3906.30   | 4636.05 | 3919.56 | 3034.83 |
| Rb      | 4666.90   | 6493.38 | 5207.21 | 3833.89 |
| Cs      | 6732.80   | 11244.92 | 7894.26 | 6008.81 |
| Cu      | 249.56    | 466.54 | 393.98 | 312.73 |
| Ag      | 342.29    | 741.72 | 441.06 | 392.27 |
| Be⁺     | 68.80     | 40.00  | 39.36 | 38.95 |
| Mg⁺     | 154.59    | 120.87 | 115.17 | 109.78 |
| Ca⁺     | 541.03    | 565.94 | 425.62 | 383.40 |
| Sr⁺     | 775.72    | 1040.23 | 667.53 | 623.11 |
| Ba⁺     | 1293.20   | 2284.40 | 1306.28 | 1348.81 |
| Be      | 213.41    | 443.51 | 273.87 | 161.69 |
| Mg      | 629.59    | 1257.52 | 750.44 | 523.40 |
| Ca      | 2188.20   | 5035.02 | 2441.13 | 1809.39 |
| Sr      | 3149.30   | 7882.73 | 3508.83 | 2750.55 |
| Ba      | 5379.60   | 15037.42 | 6184.94 | 5892.73 |
| He      | 1.46      | 1.62  | 1.43 | 1.43 |
| Ne      | 6.38      | 6.79  | 5.91 | 6.19 |
| Ar      | 64.30     | 96.28 | 54.60 | 58.57 |
| Kr      | 129.56    | 211.12 | 110.30 | 122.45 |
| Xe      | 285.87    | 537.65 | 221.15 | 275.55 |

MAPE | 62.1% | 17.7% | 16.2% |
AMAX | 179.5% | 57.9% | 43.4% |
Figure 3: Results for $C_{6}^{AA}$ for 23 atoms and ions (see table 1). The solid line depicts one-to-one correspondence of the model with the reference data obtained from ref 14. For clarity, the full range, and a reduced range are shown. The mean absolute percentage error (MAPE) for Hartree-Fock, MP2 and CCSD monomer pair densities is 62.1%, 17.7% and 16.2%, respectively.

Figure 4: Dispersion coefficients $C_{6}^{AB}$ for 253 pairs formed by selecting $A$ and $B$ from the species listed in table 1, computed using Hartree–Fock, MP2 and CCSD pair densities for the monomers with the def2-TZVPP basis set. The solid line depicts one-to-one correspondence of the model with the reference data obtained from ref 14. For clarity, the full range, and a reduced range are shown. The mean absolute percentage error (MAPE) for Hartree-Fock, MP2 and CCSD monomer pair densities is 52.3%, 12.1%, 11.9%, respectively.
4.2 Isotropic dispersion coefficients for molecules

Isotropic molecular dispersion coefficients $C_{AA}^{6}$ were computed for 26 molecules consisting mainly of first and second row elements. Our results are compared with reference values from DOSD measurements in table 2 and are also illustrated in figure 5. The MAPE using Hartree–Fock pair-density with def2-TZVPP basis is 52.5%. This comes down to 13.7% and 8.6% when using MP2 and CCSD pair-densities, respectively. This is in line with the results for the noble-gas atoms: there is now a clear systematic improvement with the level of theory of the monomer pair densities, with CCSD yielding good results with the lowest variance.

![Graph](image)

Figure 5: The isotropic dispersion coefficients $C_{AA}^{6}$ for molecules calculated using Hartree–Fock, MP2 and CCSD pair-densities and reported in table 2. The solid line depicts one-to-one correspondence of the model with the experimental data. For clarity, the full range, and a reduced range are shown.

For test set 4, we have computed isotropic dispersion coefficients $C_{AA}^{6}$ for 157 mixed molecule pairs selected from table 2. The results are illustrated in figure 6 where they are compared, again, with reference values from DOSD, measurements and are available in the supplementary material. The MAPE using Hartree–Fock, MP2 and CCSD pair densities are 57.1%, 7.9% and 7.2%, respectively.

From these calculations we can confirm that for closed-shell molecules, the Hartree–Fock
Table 2: Isotropic dispersion coefficients $\tilde{C}_6^{AA}$ for a set of molecules calculated using def2-TZVPP basis set. For each species, the dispersion coefficient closest to the reference value is in bold font.

| Species | Ref. | HF  | MP2 | CCSD |
|---------|------|-----|-----|------|
| H2      | 12.1 | 16.42 | 15.76 | 11.60 |
| C2H6    | 381.9 | 542.19 | **411.68** | 346.17 |
| C2H4    | 300.2 | 472.25 | **310.09** | 273.50 |
| C2H2    | 204.1 | 372.13 | **192.44** | 192.34 |
| H2O     | 45.3  | 55.57 | 38.88 | **40.55** |
| H2S     | 216.8 | 358.57 | 193.01 | **199.08** |
| NH3     | 89    | 114.66 | **77.58** | 77.52 |
| SO2     | 293.9 | 473.00 | 281.11 | **287.00** |
| SiH4    | 343.9 | 462.54 | **346.18** | 308.09 |
| N2      | 73.3  | 135.53 | 58.37 | **70.57** |
| HF      | 19    | 21.70 | 16.67 | **17.66** |
| HCl     | 130.4 | 201.66 | 108.00 | **115.47** |
| HBr     | 216.6 | 372.17 | 187.65 | **205.25** |
| H2CO    | 165.2 | 207.04 | **135.75** | 135.13 |
| CH4     | 129.6 | 183.70 | **128.52** | 120.00 |
| CH3OH   | 222   | 288.75 | **223.07** | 196.93 |
| CS2     | 871.1 | 2017.72 | **906.90** | 975.32 |
| CO      | 81.4  | 122.69 | 66.98 | **75.13** |
| CO2     | 158.7 | 232.44 | 153.00 | **153.45** |
| Cl2     | 389.2 | 676.48 | **384.86** | 368.85 |
| C3H6    | 662.1 | 993.49 | 769.43 | **590.50** |
| C3H8    | 768.1 | 1092.09 | 919.72 | **688.07** |
| C4H8    | 1130.2 | 1699.13 | 1527.79 | **1023.72** |
| C4H10   | 1268.2 | 1821.45 | 1714.29 | **1137.31** |
| C5H12   | 1905.0 | 2733.69 | 2872.35 | **1695.39** |
| C6H6    | 1722.7 | 3116.90 | 2148.87 | **1630.94** |

|        | MAPE | 52.1% | 13.7% | 8.6% |
|--------|------|-------|-------|------|
|        | AMAX | 131.6% | 50.8% | 18.2% |
pair density leads to consistent overestimation of the dispersion coefficients. The use of a correlated pair density (MP2 or CCSD) improves the results considerably, with CCSD providing better accuracy and lowest scattering of the results. For CCSD, 11 of the 26 $C_{6}^{AA}$ deviate from the reference value more than 10%, compared to 16 for MP2 and 26 for Hartree–Fock. With the exception of H$_2$CO, all the CCSD values are within 13% of the reference value.

Figure 6: Isotropic dispersion coefficients $C_{6}^{AB}$ for 157 mixed molecule pairs selected from table 2, calculated using Hartree–Fock (MAPE 57.1%), MP2 (MAPE 7.9%) and CCSD (MAPE 7.2%) monomer pair-densities (def2-TZVPP basis set). The solid line depicts one-to-one correspondence of the model with the experimental data. For clarity, the full range, and a reduced range are shown.

4.3 Anisotropies

To test the applicability of the method for the orientation dependence (anisotropy) of the dispersion coefficients, we performed calculations for the diatomics H$_2$, N$_2$ and CO, and interacting with noble-gas atoms. The resulting $\Gamma_{6}^{AB}$ are listed in table 3 and the resulting $\Delta_{6}^{AB}$ are listed in table 4. For both $\Gamma_{6}^{AB}$ and $\Delta_{6}^{AB}$ CCSD (MAPE 6.9%, 7.4%, respectively) performs better than MP2 (MAPE 40.3%, 58.9%), which in turn performs better
than Hartree-Fock (MAPE 111.1%, 210.2%). MP2 performs better for the pairs involving H₂ than for the pairs involving N₂ and CO.

Table 3: Anisotropic dispersion coefficients \( \Gamma_{6}^{AB} \) for the diatomics H₂, N₂ and CO, and interacting with noble-gas atoms calculated using def2-TZVPP basis set. For each species, the coefficient closest to the reference value is in bold font. The MAPE and AMAX are calculated for the product \( C_{6} \Gamma_{6}^{AB} \).

| Pairs    | Ref. | HF   | MP2   | CCSD  |
|----------|------|------|-------|-------|
| H₂−H₂    | 0.1006 | 0.1416 | 0.1099 | **0.1021** |
| H₂−N₂    | 0.1109 | 0.1350 | **0.1040** | 0.0972 |
| N₂−H₂    | 0.0966 | 0.1884 | 0.0474 | **0.1251** |
| N₂−N₂    | 0.1068 | 0.1809 | 0.0442 | **0.1211** |
| H₂−He    | 0.0924 | 0.1288 | 0.1013 | **0.0947** |
| H₂−Ne    | 0.0901 | 0.1240 | 0.0981 | **0.0920** |
| H₂−Ar    | 0.0971 | 0.1343 | 0.1046 | **0.0977** |
| H₂−Kr    | 0.0986 | 0.1369 | 0.1059 | **0.0990** |
| H₂−Xe    | 0.1005 | 0.1397 | 0.1078 | **0.1006** |
| N₂−He    | 0.1027 | 0.1738 | 0.0429 | **0.1192** |
| N₂−Ne    | 0.0999 | 0.1672 | 0.0412 | **0.1164** |
| N₂−Ar    | 0.1074 | 0.1800 | 0.0446 | **0.1214** |
| N₂−Kr    | 0.1087 | 0.1827 | 0.0452 | **0.1223** |
| N₂−Xe    | 0.1104 | 0.1856 | 0.0461 | **0.1234** |
| CO−CO    | 0.094 | 0.1013 | 0.0600 | **0.0956** |
| CO−H₂    | 0.0949 | 0.1030 | 0.0616 | **0.0970** |
| H₂−CO    | 0.0976 | 0.1350 | 0.1047 | **0.0979** |
| CO−N₂    | 0.0939 | 0.1014 | 0.0598 | **0.0954** |
| N₂−CO    | 0.1077 | 0.1808 | 0.0446 | **0.1216** |
| CO−He    | 0.0933 | 0.0997 | 0.0591 | **0.0947** |
| CO−Ne    | 0.0916 | 0.0975 | 0.0580 | **0.0933** |
| CO−Ar    | 0.0942 | 0.0975 | 0.0600 | **0.0955** |
| CO−Kr    | 0.0943 | 0.1016 | 0.0603 | **0.0958** |
| CO−Xe    | 0.0944 | 0.1021 | 0.0608 | **0.0961** |
|          | MAPE | 111.1% | 40.3% | 6.9%  |
|          | AMAX | 213.7% | 67.3% | 23.1% |

5 Conclusions and Perspectives

We have performed a first extensive exploration of the performance of the method of ref [4] to compute dispersion coefficients \( C_{6} \) using ground-state pair densities of the monomers only.
Table 4: Anisotropic dispersion coefficients $\Delta_{AB}^B$ for the diatomics $H_2$, $N_2$ and CO calculated using def2-TZVPP basis set. For each species, the coefficient closest to the reference value is in bold font. The MAPE and AMAX are calculated for the product $C_{AB}^B$.

| Pairs   | Ref. | HF    | MP2   | CCSD  |
|---------|------|-------|-------|-------|
| $H_2-H_2$ | 0.0108 | 0.0214 | 0.0128 | 0.0110 |
| $H_2-N_2$ | 0.0114 | 0.0269 | 0.0053 | 0.0126 |
| $N_2-N_2$ | 0.0121 | 0.0346 | 0.0021 | 0.0151 |
| CO-CO   | 0.0090 | 0.0104 | 0.0037 | 0.0092 |
| CO-$H_2$ | 0.0094 | 0.0142 | 0.0066 | 0.0096 |
| CO-$N_2$ | 0.0103 | 0.0188 | 0.0028 | 0.0118 |
| MAPE    | 210.2%  | 58.9%  | 7.4%   |
| AMAX    | 427.0%  | 85.9%  | 19.8%  |

The method is based on the idea of a supramolecular wavefunction that is constrained to leave the diagonal of the many-body reduced density matrix of each monomer unchanged, leading to variational equations for the dispersion coefficients that can be solved in a very efficient manner.

We have found that for closed shell species (all noble gas atoms and molecule pairs) the method yields rather accurate isotropic dispersion coefficients when using CCSD (or even MP2) monomer pair densities, with mean absolute percentage errors for CCSD for the whole closed-shell data set around 7.1% and a maximum error within 18.3%. These results obtained with CCSD pair densities have accuracy comparable to linear-response CCSD calculations within the aug-cc-pVDZ basis set on a set of closed-shell molecules (which have MAPE 6.4% and AMAX 25.7%). From the data available, the dispersion coefficients calculated using CCSD pair density also outperform XDM for both atoms and molecules. However, the DFT-D4 dispersion model has notably lower MAPE for a test set consisting of closed-shell molecules i.e. test set 3 (MAPE 2.6%, AMAX 5.8%, using the data reported in the supplementary material of ref). Other methods like TS and LRD have also a similar or slightly better performance than our formalism. We should also remark that the performance of our method is less satisfactory for open-shell atoms and ions. An advantage over methods like DFT-D4 is that our formalism also predicts the anisotropy of dispersion coefficients, which on a limited set of pairs involving diatomics and noble-gas atoms yields satisfactory
results for the anisotropy $\Gamma_6^{AB}$ (MAPE 6.9%, AMAX 23.1%) and the anisotropy $\Delta_6^{AB}$ (MAPE 7.4%, AMAX 19.8%), when using a CCSD pair density.

An attractive feature of our formalism is also that the basis set used in the monomer calculations has been found to have little effect on the computed dispersion coefficients. We believe that this study provides evidence that the method can be already used to compute dispersion coefficients for closed shell molecules, using CCSD ground-state pair densities for the monomers. The study reported here is also conceptually interesting as it shows that rather accurate results can be obtained by keeping the many-body densities of the fragments unchanged, at least for closed-shell systems.

We should also stress that the choice of the basis in which to expand the density constraint, i.e. the dispersal functions $b_i(\mathbf{r})$ of eq (2), is arbitrary and that the current choice of eq (22) is far from optimal. For some cases, the convergence with the number of dispersal functions is slow, and too high multipole moments integrals may become numerically unstable. In future works we will explore more closely the determination of an optimal choice for the dispersal functions, as we have preliminary indications that with a proper choice it is possible to use just a few of them to obtain well converged results. We will also further investigate possible ways to improve the results for open shell fragments, and we will work on building approximations based on model exchange-correlation holes from density functional theory.

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Supporting Information Available

The following files are available free of charge.

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