Supporting Information

“Local decomposition of imaginary polarizabilities and dispersion coefficients”

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1 Theory

1.1 Anisotropic Dispersion Interaction

We will here give the dispersion energy in a form which requires a few definitions in order to make the presentation self-contained. Consider two separated systems (molecules or atoms) labeled by 1 and 2. They have each a center-of-mass at a position represented by vectors $R_1$ and $R_2$, respectively, with Cartesian representations in a common coordinate system: $X_i$ and $X_2$ for $i = 1, 2, 3$. We refer to the vector connecting the two subsystems by

$$ R_{12} = R_1 - R_2 $$

(1)

i.e., the distance between the centers of mass is $R_{12} = |R_{12}|$

We use $r_1$ for an electronic coordinate associated with system 1 and $r_2$ for electrons associated with system 2. The density-density response function of system 1 is defined by

(see e.g. Ref. 1, eq 9.4.2)

$$ \langle \langle \hat{\rho}(r_1); \hat{\rho}(r_1') \rangle \rangle_\omega = \sum_{n_1 > 0} \frac{\langle \Psi_0^{(1)} | \hat{\rho}(r_1) | \Psi_{n_1}^{(1)} \rangle \langle \Psi_{n_1}^{(1)} | \hat{\rho}(r_1') | \Psi_0^{(1)} \rangle}{\hbar(\omega - \omega_{n_1}^{(1)})} - \frac{\langle \Psi_0^{(1)} | \hat{\rho}(r_1') | \Psi_{n_1}^{(1)} \rangle \langle \Psi_{n_1}^{(1)} | \hat{\rho}(r_1) | \Psi_0^{(1)} \rangle}{\hbar(\omega + \omega_{n_1}^{(1)})} $$

(2)

where $\Psi_{n_1}^{(1)}$ is a stationary state of system 1 with $n_1 = 0$ being the ground state and $\hbar \omega_{n_1}^{(1)} \equiv E_{n_1}^{(1)} - E_0^{(1)}$ is excitation energy from the ground state of system 1 to its $n_1$:th excited state. The density operator $\hat{\rho}(r_1)$ has the property that its expectation value is the electron density at a point in space. It is given in second-quantized form by expanding it in a given basis set on system 1, $\{ \phi_p^{(1)}(r_1) \}_{p=1}^\infty$:

$$ \hat{\rho}(r_1) = \sum_{pq} \phi_p^{(1)}(r_1)^* \phi_q^{(1)}(r_1) (a_{p\alpha}^\dagger a_{q\alpha} + a_{p\beta}^\dagger a_{q\beta}) $$

(3)

where $a_{p\alpha}^\dagger a_{q\alpha}$ is an operator representing an excitation of an $\alpha$-electron (spin $+\frac{1}{2}$) from orbital $q$ to $p$ and $a_{p\beta}^\dagger a_{q\beta}$ the equivalent for a $\beta$-electron (spin $-\frac{1}{2}$).
In particular the dispersion energy of two interacting molecules (denoted by 1 and 2) is given by

\[ E_{\text{disp}} = -\frac{\hbar}{2\pi} \int \int dr_1 dr_2 \frac{1}{r_{12}} \int \int dr'_1 dr'_2 \frac{1}{r'_{12}} \int_0^\infty d\omega \langle \hat{\rho}(r_1); \hat{\rho}(r'_1) \rangle \langle \hat{\rho}(r_2); \hat{\rho}(r'_2) \rangle \]  

(4)

where the linear response functions are evaluated at an imaginary frequency \( i\omega \). The intermolecular Coulomb potential can further be expanded in multipole moments, e.g., in solid spherical harmonics. Another alternative is a real-valued Taylor expansion to obtain the Cartesian moments, by expanding around the intermolecular distance vector. Introducing the electronic coordinate vectors relative to the local molecular coordinate frames (see Fig.S1) \( r_{1;1} = r_1 - R_1 \) and \( r_{2;2} = r_2 - R_2 \) we have

\[ r_{12} = r_{1;1} - r_{2;2} + R_{12} \]  

(5)

Figure S1: Definition of coordinates in section 2.1

When the first two terms are small compared to the last, as we can assume for long-range
intermolecular interactions, we may expand the Coulomb potential in a Taylor series

\[
\frac{1}{r_{12}} = \frac{1}{|\mathbf{r}_{1;1} - \mathbf{r}_{2;2} + \mathbf{R}_{12}|} = \sum_{n=0}^{\infty} \frac{1}{n!} \left( (\mathbf{r}_{1;1} - \mathbf{r}_{2;2}) \cdot \nabla R_{12} \right)^n \frac{1}{R_{12}}
\]

(6)

where the derivative operator only acts on the internuclear distance

\[
\nabla R_{12} = \left( \frac{\partial}{\partial X_{12}^1}, \frac{\partial}{\partial X_{12}^2}, \frac{\partial}{\partial X_{12}^3} \right)
\]

(7)

Furthermore we can use the binomial theorem to obtain

\[
\left( (\mathbf{r}_{1;1} - \mathbf{r}_{2;2}) \cdot \nabla R_{12} \right)^n = \sum_{k=0}^{n} \binom{n}{k} \left( (\mathbf{r}_{1;1} \cdot \nabla R_{12})^k (\mathbf{r}_{2;2} \cdot \nabla R_{12})^{n-k} \right)
\]

(8)

Substituting expansions in Eqs. 6 and 8 in the linear response function in Eq. 2, we can rewrite Eq. 4 as

\[
E_{\text{disp}} = -\frac{\hbar}{2\pi} \sum_{nk} \sum_{n'k'} \frac{1}{n!n'!} \binom{n}{k} \binom{n'}{k'} (-1)^{n-k+n'-k'} \times \\
\int_0^\infty d\omega \left\langle \int d\mathbf{r}_1 \hat{\rho}(\mathbf{r}_1)(\mathbf{r}_{1;1} \cdot \nabla R_{12})^k; \int d\mathbf{r}_2 \hat{\rho}(\mathbf{r}_2')(\mathbf{r}_{1;1}' \cdot \nabla R_{12}')^{k'} \right\rangle \omega \times \\
\left\langle \int d\mathbf{r}_1' \hat{\rho}(\mathbf{r}_1') (\mathbf{r}_{2;2} \cdot \nabla R_{12})^{n-k}; \int d\mathbf{r}_2' \hat{\rho}(\mathbf{r}_2') (\mathbf{r}_{2;2}' \cdot \nabla R_{12}')^{n'-k'} \right\rangle \omega \frac{1}{R_{12} R_{12}'} \bigg|_{R_{12}=R_{12}'}
\]

(9)

where we can identify linear response functions of second-quantized formulations of multipole moments of various orders.

The lowest non-vanishing term is with \( k = k' = 1 \) and \( n = n' = 2 \), where we have electrical dipole operators

\[
\hat{\mathbf{r}} = \int d\mathbf{r} \hat{\rho}(\mathbf{r}) \mathbf{r}
\]

(10)
and we can identify the well-known expression for dipole-dipole polarizabilities

\[ \alpha(i\omega) = -\langle \hat{\mathbf{r}}; \hat{\mathbf{r}} \rangle_{i\omega} \]  

This expansion for a specific orientation of the molecules is an expression which couples the molecular polarizability tensors with second derivatives of the intermolecular distance and which decays as \( R_{12}^{-6} \)

\[ E_{\text{disp}} \approx -\frac{\hbar}{2\pi} \int_{0}^{\infty} d\omega \sum_{ijkl} \alpha_{ij}^{(1)}(i\omega)\alpha_{kl}^{(2)}(i\omega)T_{ik}T_{jl} \]  

where the summation is over cartesian coordinates in a common coordinate system, and \( T \) is the second-order derivative of the Coulomb potential

\[ T_{ik} = \frac{\partial^2}{\partial X_{12}^i \partial X_{12}^k} \frac{1}{R_{12}} = \frac{3X_{12}^i X_{12}^k - \delta_{ik} R_{12}^5}{R_{12}^5} \]  

1.2 Isotropic dispersion coefficient \( C_6 \)

An isotropic expression for the dispersion energy is obtained by rotational averaging of the two subsystems independently. Molecular tensors such as polarizabilities are usually calculated in a coordinate system fixed by molecular nuclei (body-fix axes) whereas observations are carried out in a coordinate system defined by the observer (lab-fix axes). With \( C_{\mu i} \) as the transformation matrix between body-fix (greek indices) and space-fix (roman indices) axes this averaging may be written

\[ E_{\text{disp}}^{\text{iso}} \approx -\frac{\hbar}{2\pi} \int_{0}^{\infty} d\omega \sum_{ijkl \ \mu \nu \ \sigma \tau} \alpha_{\mu \nu}^{(1)}(i\omega)\alpha_{\sigma \tau}^{(2)}(i\omega)C_{\mu i}C_{\nu j}C_{\sigma k}C_{\tau l}T_{ik}T_{jl} \]
Detailed expressions for rotational averages of tensors can be found, e.g., in Ref. 2; in our case the average can be written as

$$C_{\mu i} C_{\nu j} = \frac{1}{3} \delta_{\mu \nu} \delta_{ij} \quad (15)$$

Substituting with the isotropic polarizabilities

$$\bar{\alpha} = \frac{1}{3} \sum_k \alpha_{kk} \quad (16)$$

we obtain

$$E_{\text{disp}}^{\text{iso}}(R_{12}) = -\frac{\hbar}{2\pi} \int_0^\infty \bar{\alpha}^{(1)}(i\omega)\bar{\alpha}^{(2)}(i\omega) \sum_{ik} T_{ik} T_{ik}$$

$$= -\frac{\hbar}{2\pi} \int_0^\infty \bar{\alpha}^{(1)}(i\omega)\bar{\alpha}^{(2)}(i\omega) \frac{6}{R_{12}^6}$$

$$= -\frac{3h}{\pi} \int_0^\infty \bar{\alpha}^{(1)}(i\omega)\bar{\alpha}^{(2)}(i\omega) d\omega \frac{1}{R_{12}^6}$$

$$\equiv -\frac{C_6}{R_{12}^6} \quad (17)$$

which defines the well-known $C_6$ coefficient for the dispersion interaction. By decomposing the molecular polarizabilities $\alpha^{(1)}$ and $\alpha^{(2)}$ into distributed atomic contributions $\alpha^{(1)}_i$ and $\alpha^{(2)}_j$, respectively, where $i$ is an atomic site in molecule 1 and $j$ an atomic site in molecule 2, the atom-atom dispersion coefficient $C_6^{ij}$ for atoms $i$ and $j$ can be written as

$$C_6^{ij} = \frac{3h}{\pi} \int_0^\infty \bar{\alpha}^{(1)}_i(i\omega)\bar{\alpha}^{(2)}_j(i\omega) d\omega \quad (18)$$

where now the distributed polarizabilities for the atoms contributes to the atomic $C_6^{ij}$ dispersion. Note that in order to calculate the total dispersion energy by our scheme LoProp (see below), each atom-atom pair has to be evaluated. For a water dimer with 3 atoms in each molecule, there is thus $3 \times 3 = 9$ atom-pairs to consider. This is due to the LoProp polarizability being additive and summing up to the molecular polarizability, and the sum
of all LoProp $C_{ij}^6$ elements being equal to the molecular $C_6$.

# 2 Basis set dependence

Table S1: Cartesian coordinates (in Å) of formaldehyde optimized at the B3LYP/6-31++G** level

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<thead>
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<th></th>
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<tr>
<td>C</td>
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<td>-0.000208</td>
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Table S2: Cartesian coordinates (in Å) of formamide optimized at the B3LYP/6-31++G** level

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Table S3: Cartesian coordinates (in Å) of glycine optimized at the B3LYP/6-31++G** level

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</table>
3 Diatomics

3.1 H2 dimer

Table S4: Reference structure in Cartesian coordinates (Å). Bond length was taken from experiment.

\[
\begin{array}{ccc}
H & 0.00000 & 0.00000 & -0.37070 \\
H & 0.00000 & 0.00000 & 0.37070
\end{array}
\]
Figure S2: Scatter plots of the dispersion energy for the H₂–H₂ dimers calculated with the anisotropic molecular and LoProp models versus the reference dispersion energy obtained with SAPT2+/aug-cc-pVTZ.
Figure S3: Scatter plots of the dispersion energy for the H$_2$–H$_2$ dimers calculated with the anisotropic molecular and LoProp models versus the reference dispersion energy obtained with SAPT2+/aug-cc-pVTZ.
### 3.2 N2 dimer

Table S5: Reference structure in Cartesian coordinates (Å). Bond length was taken from experiment.

\[
\begin{array}{ccc}
\text{N} & 0.00000 & 0.00000 & 0.55256 \\
\text{N} & 0.00000 & 0.00000 & -0.55256 \\
\end{array}
\]
Figure S4: Scatter plots of the dispersion energy for the \( \text{N}_2-\text{N}_2 \) dimers calculated with the anisotropic molecular and LoProp models versus the reference dispersion energy obtained with SAPT2+/aug-cc-pVTZ.
Figure S5: Scatter plots of the dispersion energy for the N$_2$–N$_2$ dimers calculated with the anisotropic molecular and LoProp models versus the reference dispersion energy obtained with SAPT2+/aug-cc-pVTZ.
3.3 CO dimer

Table S6: Reference structure in Cartesian coordinates (Å). Bond length was taken from experiment.

\[
\begin{array}{ccc}
\text{C} & 0.00000 & 0.00000 & -0.56400 \\
\text{O} & 0.00000 & 0.00000 & 0.56400 \\
\end{array}
\]
Figure S6: Scatter plots of the dispersion energy for the CO–CO dimers calculated with the anisotropic molecular and LoProp models versus the reference dispersion energy obtained with SAPT2+/aug-cc-pVTZ.
Figure S7: Scatter plots of the dispersion energy for the CO–CO dimers calculated with the anisotropic molecular and LoProp models versus the reference dispersion energy obtained with SAPT2+/aug-cc-pVTZ.
4 Benzene dimer

Table S7: Cartesian coordinates (in Å) for benzene optimized at the B3LYP/6-31++G** level

\[
\begin{array}{ccc}
\text{H} & -0.896118 & 0.000000 -0.517374 \\
\text{H} & 1.255737 & 0.000000 -1.759748 \\
\text{H} & 3.407591 & 0.000000 -0.517374 \\
\text{H} & 3.407591 & 0.000000 1.967374 \\
\text{H} & 1.255737 & 0.000000 3.209748 \\
\text{H} & -0.896118 & 0.000000 1.967374 \\
\text{C} & 0.044748 & 0.000000 0.025835 \\
\text{C} & 0.044748 & 0.000000 1.424165 \\
\text{C} & 1.255737 & 0.000000 -0.673330 \\
\text{C} & 1.255737 & 0.000000 2.123330 \\
\text{C} & 2.466726 & 0.000000 0.025835 \\
\text{C} & 2.466726 & 0.000000 1.424165 \\
\end{array}
\]

5 Methane dimer

Table S8: Cartesian coordinates (in Å) for methane optimized at the B3LYP/6-31++G** level

\[
\begin{array}{ccc}
\text{H} & -0.000017 & 0.000031 1.092768 \\
\text{C} & 0.000030 & -0.000009 -0.000034 \\
\text{H} & -0.555621 & 0.867583 -0.364388 \\
\text{H} & 1.029263 & 0.047391 -0.364261 \\
\text{H} & -0.473465 & -0.915066 -0.364315 \\
\end{array}
\]

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Figure S8: Molecular isotropic (a), molecular anisotropic (b), LoProp isotropic (c) and LoProp anisotropic (d) dispersion interaction energies for the CH$_4$–CH$_4$ dimer as a function of monomer distances.
6 Pyridine dimer

Table S9: Cartesian coordinates (in Å) for pyridine optimized at the B3LYP/6-31++G**

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References


Figure S9: Molecular isotropic (a), molecular anisotropic (b), LoProp isotropic (c) and LoProp anisotropic (d) dispersion interaction energies for the pyridine–pyridine dimer as a function of monomer distances.