Dispersion forces between linear molecules

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The coefficients of the $R^{-4}$ and $R^{-3}$ terms in the series representation of the dispersion interaction between two hydrogen molecules and between two nitrogen molecules are calculated by a simple variation method. The agreement with available calculations is encouraging.

I. INTRODUCTION

The anisotropy of the dispersion interaction plays a role in many phenomena such as orientational ordering, librational motion, and rotational relaxation processes. For the leading term which is due to the dipole-dipole interaction, London presented a simple approximate expression which connects the anisotropic dispersion interaction parameters with the anisotropy of the static polarizability. Starting from the Casimir–Polder integral formula, more refined theoretical and semi-empirical calculations of the dipole dispersion forces between linear molecules have been undertaken. Recently Meyer and Mulder et al. have calculated in addition to the $R^{-5}$ (dipole) contribution the $R^{-6}$ and $R^{-8}$ terms in the series representation between two hydrogen molecules and between two nitrogen molecules, using sum over transition moments techniques. It is the purpose of the present paper to show that the simple Kirkwood variation method yields results for the higher order dispersion interactions between linear molecules that agree rather well with the elaborate calculations mentioned above.

II. DISPERSION INTERACTION AND DYNAMIC POLARIZABILITIES

Expanding the interaction potential between two linear molecules $A$ and $B$ in a multipole series and using second order perturbation theory one obtains for the dispersion energy a result that can be written in the form

$$U_{\text{disp}} = -\sum_{L_a,L_b} C_{L_a,L_b} Y_{L_a,L_b}(\theta_a, \phi_a) Y_{L_b,L_a}(\theta_b, \phi_b).$$

(1)

The polar angles $(\theta_a, \phi_a)$ and $(\theta_b, \phi_b)$ that define the orientation of the axes of cylindrical symmetry of the molecules $A$ and $B$ are measured relative to a Cartesian coordinate system the $z$ axis of which coincides with the line connecting the centers of mass of the two molecules. For a given value of $L$, the summation over the indices $L_a$ and $L_b$ is limited by the triangle condition. The coefficients $C_{L_a,L_b}$ can be expressed in terms of integrals of products of dynamic multipole polarizabilities $\alpha_{\mu \nu}$, which are defined and calculated in Sec. III, evaluated at imaginary frequencies. The coefficient specifying the isotropic part of the $R^{-4}$ term reads

$$C(110;110;0) = \frac{1}{3\pi} \int_0^\infty \left\{ \alpha_0^2(\xi) + 2\alpha_1^2(\xi) \right\}^2 d\xi.$$

The coefficients associated with the orientational dependent part of the $R^{-4}$ term are given by

$$C(110;112;0) = \frac{1}{3\pi} \int_0^\infty \left\{ \alpha_0^2(\xi) + 2\alpha_1^2(\xi) \right\} \left\{ \alpha_1^2(\xi) - \alpha_1^1(\xi) \right\} d\xi,$$
$$C(112;110;0) = \frac{1}{2\pi} \int_0^\infty \left\{ \alpha_0^2(\xi) - \alpha_1^1(\xi) \right\}^2 d\xi.$$

The $R^{-5}$ term contains a contribution due to the dipole–quadrupole interaction ("quadratic terms") and contributions that are due to the mixing of the dipole–dipole interaction and the dipole–octopole term ("cross terms"). The isotropic part is exclusively due to the dipole–quadrupole interaction

$$C(110;220;0) = \frac{1}{2\pi} \int_0^\infty \left\{ \alpha_2^2(\xi) + 2\alpha_1^2(\xi) \right\} \left\{ \alpha_2^2(\xi) + 2\alpha_1^2(\xi) + 2\alpha_3^2(\xi) \right\} d\xi.$$

The orientational dependent part of the $R^{-5}$ term that originates from the dipole–quadrupole interaction is specified by the following coefficients:

$$C(110;222;0) = \frac{4}{\pi} \int_0^\infty \left\{ \alpha_1^0(\xi) + 2\alpha_1^2(\xi) \right\} \left\{ \alpha_2^2(\xi) + \alpha_2^2(\xi) - 2\alpha_2^2(\xi) \right\} d\xi,$$
$$C(110;224;0) = \frac{1}{\pi} \int_0^\infty \left\{ \alpha_1^0(\xi) + 2\alpha_1^2(\xi) \right\} \left\{ 3\alpha_2^2(\xi) - 4\alpha_2^2(\xi) + \alpha_3^2(\xi) \right\} d\xi.$$
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\[ C(112; 220; 0) = \frac{2}{5\pi} \int_0^\infty \left[ \alpha_{11}^0(i\xi) - \alpha_{11}^0(i\xi) \right] \left[ \alpha_{22}^0(i\xi) + 2\alpha_{22}^0(i\xi) + 2\alpha_{22}^0(i\xi) \right] d\xi, \]

\[ C(112; 222; 0) = \frac{3}{2} C(112; 222; \pm 1) = \frac{3}{2} C(112; 222; \pm 2) = \frac{5}{7\pi} \int_0^\infty \left[ \alpha_{11}^0(i\xi) - \alpha_{11}^0(i\xi) \right] \left[ \alpha_{22}^0(i\xi) + \alpha_{22}^0(i\xi) - 2\alpha_{22}^0(i\xi) \right] d\xi, \]

\[ C(112; 224; 0) = \frac{22}{3\sqrt{3} \pi} C(112; 224; \pm 1) = \frac{11}{13} C(112; 224; \pm 2) = \frac{22}{3\sqrt{3} \pi} \int_0^\infty \left[ \alpha_{11}^0(i\xi) - \alpha_{11}^0(i\xi) \right] \left[ \alpha_{22}^0(i\xi) - 4\alpha_{22}^0(i\xi) + \alpha_{22}^0(i\xi) \right] d\xi. \]

The mixed dipole-dipole, dipole-octopole interaction gives rise to the following anisotropic dispersion interaction coefficients

\[ C(110; 132; 0) = \frac{6}{7\pi} \int_0^\infty \left[ \alpha_{11}^0(i\xi) + 2\alpha_{11}^0(i\xi) \right] \left[ \alpha_{11}^0(i\xi) + \frac{2\sqrt{3}}{3} \alpha_{11}^0(i\xi) \right] d\xi, \]

\[ C(110; 134; 0) = \frac{10}{21\pi} \int_0^\infty \left[ \alpha_{11}^0(i\xi) + 2\alpha_{11}^0(i\xi) \right] \left[ \alpha_{11}^0(i\xi) - \frac{\sqrt{3}}{2} \alpha_{11}^0(i\xi) \right] d\xi, \]

\[ C(112; 132; 0) = 3C(112; 132; \pm 1) = -6C(112; 132; \pm 2) = \frac{6}{7\pi} \int_0^\infty \left[ \alpha_{11}^0(i\xi) - \alpha_{11}^0(i\xi) \right] \left[ \alpha_{11}^0(i\xi) + \frac{2\sqrt{3}}{3} \alpha_{11}^0(i\xi) \right] d\xi, \]

\[ C(112; 134; 0) = \frac{38}{5\sqrt{3} \pi} C(112; 134; \pm 1) = \frac{38}{3\sqrt{15} \pi} C(112; 134; \pm 2) = \frac{38}{21\pi} \int_0^\infty \left[ \alpha_{11}^0(i\xi) - \alpha_{11}^0(i\xi) \right] \left[ \alpha_{11}^0(i\xi) - \frac{\sqrt{3}}{2} \alpha_{11}^0(i\xi) \right] d\xi. \]

Thus the calculation of the dispersion interaction between linear molecules can be reduced to the calculation of the appropriate dynamic multipole polarizabilities \( \alpha_{11}^m(\omega) \).

### III. VARIATIONAL CALCULATION OF DYNAMIC POLARIZABILITIES

Consider a molecule placed in an external time-dependent field. This leads to the appearance in the Hamiltonian of a perturbation operator that can be written as

\[ V(t) = -\sum_{\text{ion}} \left( f_{0m} Q_{0m}^* e^{iwt} + f_{1m} Q_{1m} e^{-iwt} \right). \]

The multipole operator \( Q_{1m} \) is defined as

\[ Q_{1m} = +\sqrt{4/2i+1} \sum_{i=1}^n r_i Y_{1m} (\theta_i, \phi_i), \]

where the summation runs over the electrons of the system. Owing to the presence of the perturbation the expectation value of the multipole changes. In first approximation (linear response) this can be expressed in the form

\[ \langle \tilde{Q}_{1m} \rangle = \sum_{\text{ion}} \alpha_{11}^m(\omega) f_{1m} e^{iwt}. \]

Here \( \langle \cdots \rangle \) indicates an expectation value with respect to the perturbed wave function and

\[ \tilde{Q}_{1m} = Q_{1m} - \langle Q_{1m} \rangle, \]

where \( \langle Q_{1m} \rangle \) is the expectation value of \( Q_{1m} \) in the unperturbed state. The dynamic multipole polarizabilities can be calculated from

\[ \alpha_{11}^m(\omega) = \langle \phi_{0} | \tilde{Q}_{1m} | \chi_{1m}(\omega) + \chi_{1m}(-\omega) \rangle, \]

where \( \chi_{1m}(\omega) \) is determined by the first order perturbation equation

\[ (H_0 - E_0 + \omega) \chi_{1m}(\omega) - Q_{1m} \psi_0 = 0. \]

Formally this equation can be solved by expanding \( \chi_{1m}(\omega) \) in the eigenfunctions of \( H_0 \). One then obtains

\[ \alpha_{11}^m(\omega) = \sum_{\text{ion}} \frac{f_{1m}^* \psi_0}{\omega - \omega^2}. \]

where the oscillator strength \( f_{1m}^* \psi_0 \) is given by

\[ f_{1m}^* \psi_0 = 2\omega \psi_0 \langle \phi_0 | Q_{1m} | \phi_0 \rangle \langle \tilde{Q}_{1m} | \tilde{Q}_{1m} | \psi_0 \rangle. \]

Equations (8) and (7) form the basis of the sum over states techniques used in Refs. 6–8. An alternative way of calculating \( \alpha_{11}^m(\omega) \) is provided by the variational principle according to which solving the differential equation (5) is equivalent to minimizing the functional

\[ L[\chi_{1m}(\omega)] = \langle \chi_{1m}(\omega) | (H_0 - E_0 + \omega) \chi_{1m}(\omega) \rangle - \langle \chi_{1m}(\omega) | Q_{1m}^* | \psi_0 \rangle - \langle \psi_0 | Q_{1m}^* | \chi_{1m}(\omega) \rangle, \]

with respect to variations of \( \chi_{1m}(\omega) \).

Following Kirkwood\(^9\) we choose a trial function of the form

\[ \chi_{1m}(\omega) = \sum_{\text{ion}} C_{1m}^\nu_{1m} (\omega) \bar{Q}_{1m} \psi_0, \]

the \( C_{1m}^\nu_{1m}(\omega) \) being variation parameters. Minimizing \( L \) with respect to these parameters yields

\[ C_{1m}^\nu_{1m}(\omega) = [N^{-1} \mathbf{M} + \omega I_{1m}]^{-1}, \]

where the matrices \( \mathbf{M} \) and \( \mathbf{N} \) are given by

\[ M_{1m}^\nu_{1m} = \langle \phi_0 | Q_{1m} (H_0 - E_0) \bar{Q}_{1m}^* | \psi_0 \rangle + \langle \psi_0 | Q_{1m} (H_0 - E_0) \bar{Q}_{1m}^* | \psi_0 \rangle, \]

\[ N_{1m}^\nu_{1m} = 2 \langle \phi_0 | Q_{1m} \bar{Q}_{1m}^* | \psi_0 \rangle. \]

Substituting the variationally determined function \( \chi_{1m}(\pm \omega) \) in Eq. (4), one obtains

\[ \alpha_{11}^m(\omega) = \frac{3}{2} [\mathbf{N}(\mathbf{C}(\omega) + \mathbf{C}(-\omega))]_{1m}. \]

Using elementary matrix theory\(^12\) one can write the dynamic multipole polarizabilities given by Eq. (13) in the form

\[ J. Chem. Phys., Vol. 71, No. 8, 15 October 1979 \]
SJi.(-l). Indeed
polarizabilities satisfy the sum rules $S_i^m(\omega)$ and corresponding residue matrices. Although of course
the
where $(A_i^m)^\dagger$ are the eigenvalues of $N^\dagger M$ and $R^{(n)}_{i,l}$
Here the strength factors are given by

\begin{equation}
\alpha_i^m(\omega) = \sum_n \frac{(Z_i^m)_{i,l}}{(\Delta_i^m)^\dagger_{i,l} - \omega^2},
\end{equation}

Here the strength factors are given by

\begin{equation}
(Z_i^m)_\mu = (\Delta_i^m)_{\mu,l} [N R^{(n)}_{i,l}],
\end{equation}

where $(\Delta_i^m)^\dagger_{i,l}$ are the eigenvalues of $N^\dagger M$ and $R^{(n)}_{i,l}$ the
corresponding residue matrices. Although of course approximations, the variationally determined dynamic
polarizabilities satisfy the sum rules $S_i^m(0)$ and $S_i^m(-1)$. Indeed.

**TABLE II.** Static multipole polarizabilities for $H_2$ and $N_2$ (in a.u.).

<table>
<thead>
<tr>
<th></th>
<th>Present work</th>
<th>Mulder et al.</th>
<th>Meyer</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>$\alpha_i^m$</td>
<td>$\alpha_i^m$</td>
<td>$\alpha_i^m$</td>
</tr>
<tr>
<td>$\alpha_{11}^0$</td>
<td>5.59</td>
<td>7.33</td>
<td>6.44</td>
</tr>
<tr>
<td>$\alpha_{11}^1$</td>
<td>3.62</td>
<td>4.93</td>
<td>4.57</td>
</tr>
<tr>
<td>$\alpha_{22}^0$</td>
<td>14.0</td>
<td>17.99</td>
<td>17.75</td>
</tr>
<tr>
<td>$\alpha_{22}^1$</td>
<td>12.8</td>
<td>17.13</td>
<td>16.97</td>
</tr>
<tr>
<td>$\alpha_{22}^2$</td>
<td>10.1</td>
<td>14.33</td>
<td>13.85</td>
</tr>
<tr>
<td>$\alpha_{13}^0$</td>
<td>3.31</td>
<td>3.93</td>
<td>3.90</td>
</tr>
<tr>
<td>$\alpha_{13}^1$</td>
<td>2.69</td>
<td>2.88</td>
<td>2.88</td>
</tr>
<tr>
<td>$\alpha_{13}^2$</td>
<td>1.63</td>
<td>15.7</td>
<td>15.7</td>
</tr>
<tr>
<td>$\alpha_{13}^3$</td>
<td>8.28</td>
<td>8.76</td>
<td>8.76</td>
</tr>
<tr>
<td>$\alpha_{13}^4$</td>
<td>69.4</td>
<td>64.7</td>
<td>64.7</td>
</tr>
<tr>
<td>$\alpha_{13}^5$</td>
<td>71.3</td>
<td>66.0</td>
<td>66.0</td>
</tr>
<tr>
<td>$\alpha_{13}^6$</td>
<td>35.4</td>
<td>28.2</td>
<td>28.2</td>
</tr>
<tr>
<td>$\alpha_{13}^7$</td>
<td>16.1</td>
<td>22.0</td>
<td>22.0</td>
</tr>
<tr>
<td>$\alpha_{13}^8$</td>
<td>27.1</td>
<td>27.2</td>
<td>27.2</td>
</tr>
</tbody>
</table>

For hydrogen the values presented by Meyer are the
most accurate and we see that the results obtained here lie somewhat below these values which is due to the
variational character of our calculation. In Table III we present the dispersion force coefficients $C_{L_{1}L_{2}}^{L_{3}M}$
that are calculated using the formulae given in Sec. II with the dynamic polarizabilities given in Table I. In order to compare our results with Meyer and Mulder et al., it is useful to write the dispersion in-
teraction in the following form:

\begin{equation}
U_{\text{disp}} = - \sum_{L_{1}L_{2}} C_{L_{1}L_{2}}^{L_{3}M} \sum_{M_{1}} \sum_{M_{2}} \gamma_{L_{1}L_{2}M_{1}M_{2}}^{L_{3}M} \cos[M_{1} \phi_{1} - M_{2} \phi_{2}],
\end{equation}

where $\gamma_{L_{1}L_{2}M_{1}M_{2}}^{L_{3}M} = 1$. The isotropic interaction coefficients
$C_{6}$ and $C_{8}$ are given by

\begin{equation}
C_{6} = C(110;110;0),
\end{equation}

\begin{equation}
C_{8} = 2C(110;220;0).
\end{equation}

The dipole anisotropic parameters $\gamma_{L_{1}L_{2}M}^{L_{3}M}$ can be written as
TABLE IV. Anisotropic dispersion interaction parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Present Work</th>
<th>Mulder et al.</th>
<th>Meyer</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma_{200} )</td>
<td>0.113</td>
<td>0.120</td>
<td>0.109</td>
</tr>
<tr>
<td>( \gamma_{220} )</td>
<td>0.043</td>
<td>0.044</td>
<td>0.031</td>
</tr>
<tr>
<td>( \gamma_{200}^{\text{quadr}} )</td>
<td>0.102</td>
<td>0.691</td>
<td>0.089</td>
</tr>
<tr>
<td>( \gamma_{200}^{\text{cross}} )</td>
<td>0.173</td>
<td>0.159</td>
<td>0.085</td>
</tr>
<tr>
<td>( \gamma_{200}^{\text{quadr}} )</td>
<td>0.276</td>
<td>0.250</td>
<td>0.230</td>
</tr>
<tr>
<td>( \gamma_{210}^{\text{quadr}} )</td>
<td>0.016</td>
<td>0.013</td>
<td>0.0124</td>
</tr>
<tr>
<td>( \gamma_{220}^{\text{cross}} )</td>
<td>0.039</td>
<td>0.038</td>
<td>0.038</td>
</tr>
<tr>
<td>( \gamma_{220}^{\text{quadr}} )</td>
<td>0.055</td>
<td>0.051</td>
<td>0.051</td>
</tr>
<tr>
<td>( \gamma_{400}^{\text{quadr}} )</td>
<td>0.0018</td>
<td>-0.00051</td>
<td>0.0002</td>
</tr>
<tr>
<td>( \gamma_{400}^{\text{cross}} )</td>
<td>0.0073</td>
<td>0.00514</td>
<td>0.00514</td>
</tr>
<tr>
<td>( \gamma_{420}^{\text{quadr}} )</td>
<td>0.0091</td>
<td>0.0091</td>
<td>0.0046</td>
</tr>
<tr>
<td>( \gamma_{420}^{\text{cross}} )</td>
<td>0.0099</td>
<td>-0.00025</td>
<td>-0.00025</td>
</tr>
<tr>
<td>( \gamma_{420}^{\text{cross}} )</td>
<td>0.0026</td>
<td>0.00231</td>
<td>0.00231</td>
</tr>
<tr>
<td>( \gamma_{424}^{\text{quadr}} )</td>
<td>0.0045</td>
<td>0.0021</td>
<td>0.0021</td>
</tr>
<tr>
<td>( \gamma_{424}^{\text{cross}} )</td>
<td>0.0045</td>
<td>0.0021</td>
<td>0.0021</td>
</tr>
</tbody>
</table>

\( \gamma_{200}^{\text{quadr}} = C(112; 110; 0)/C_6 \),

\( \gamma_{220}^{\text{quadr}} = -3/2 \gamma_{221}^{\text{quadr}} = 36/2 = C(112; 112; 0)/C_6 \).

The anisotropy factors \( \gamma_{200}^{\text{quadr}} \) and \( \gamma_{220}^{\text{quadr}} \) are the sum of the contributions of the dipole-quadrupole interaction (quadratic terms) and the contribution of the mixed dipole-dipole, dipole octupole interaction (cross terms)

\[ \gamma_{200}^{\text{quadr}} = \gamma_{200}^{\text{quadr}} + \gamma_{200}^{\text{cross}} \]

The quadratic terms can be written as

\[ \gamma_{200}^{\text{quadr}} = (C(112; 220; 0) + C(110; 222; 0))/C_8 \],

\[ \gamma_{220}^{\text{quadr}} = -5\gamma_{221}^{\text{quadr}} = 2C(112; 222; 0)/C_8 \],

\[ \gamma_{400}^{\text{quadr}} = C(110; 224; 0)/C_8 \],

\[ \gamma_{420}^{\text{quadr}} = -2/3 \gamma_{421}^{\text{quadr}} = 123(112; 224; 0)/C_8 \].

The cross terms can be written as

\[ \gamma_{200}^{\text{cross}} = 2C(110; 132; 0)/C_8 \],

\[ \gamma_{220}^{\text{cross}} = -2\gamma_{221}^{\text{cross}} = -7\gamma_{222}^{\text{cross}} = 4C(112; 132; 0)/C_8 \],

\[ \gamma_{400}^{\text{cross}} = 2C(110; 134; 0)/C_8 \],

\[ \gamma_{420}^{\text{cross}} = 3/7 \gamma_{421}^{\text{cross}} = 152(112; 134; 0)/C_8 \].

In Table IV we present the anisotropy parameters

\[ \gamma_{200}^{\text{quadr}} (n = 6, 8) \) and compare them with the results obtained by Meyer (who only calculated the quadratic terms) and Mulder et al. We see that the overall agreement is indeed satisfactory except in the case of the \( \gamma_{200}^{\text{quadr}} \) and \( \gamma_{220}^{\text{quadr}} \) terms for the \( \text{H}_2 \) interaction where these are large differences between all three sets of values.

To conclude we see that the generalized Kirkwood method used here yields results for the higher order anisotropic dispersion interaction parameters that are of comparable accuracy as those provided by sum over states procedures.

ACKNOWLEDGMENTS

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\(^4\) H. B. G. Casimir and D. Polder, Phys. Rev. 73, 360 (1948).


\(^7\) F. Mulder, A. Van der Avoird, and P. E. S. Wormer, Mol.

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9J. G. Kirkwood, Physik. Z. 33, 57 (1932).
15The required moments for the nitrogen molecule were calculated by Dr. F. Mulder, Katholieke Universiteit Nijmegen (The Netherlands) from a SCF wave function using basis set $E''$ of Ref. 8.