

Dispersion forces between linear molecules

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The coefficients of the R^{-6} and R^{-8} 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.¹ For the leading term which is due to the dipole-dipole interaction, London² presented a simple approximate expression which connects the anisotropic dispersion interaction parameters with the anisotropy of the static polarizability.³ Starting from the Casimir-Polder integral formula⁴ more refined theoretical and semi-empirical calculations of the dipole dispersion forces

between linear molecules have been undertaken.⁵

Recently Meyer⁶ and Mulder *et al.*^{7,8} have calculated in addition to the R^{-6} (dipole) contribution the R^{-8} and R^{-10} terms in the series representation between two hydrogen molecules^{6,7} and between two nitrogen molecules,⁸ using sum over transition moments techniques. It is the purpose of the present paper to show that the simple Kirkwood variation method⁹ 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 series¹⁰ and using second order perturbation theory one obtains for the dispersion energy a result that can be written in the form

$$U_{\text{disp}} = - \sum_{L_a, L_b} \sum_{M = \min(L_a, L_b)}^{+\infty} \sum_{l_a, l'_a, l_b, l'_b} \frac{C(l_a, l'_a, L_a; l_b, l'_b, L_b; M)}{R^{(l_a + l'_a + l_b + l'_b + 2)}} \frac{4\pi}{\sqrt{(2L_a + 1)(2L_b + 1)}} Y_{L_a M}(\theta_a, \varphi_a) Y_{L_b - M}(\theta_b, \varphi_b). \quad (1)$$

The polar angles (θ_a, φ_a) and (θ_b, φ_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_a the summation over the indices l_a and l'_a is limited by the triangle condition. The coefficients $C(l_a, l'_a, L_a; l_b, l'_b, L_b; M)$ can be expressed in terms of integrals of products of dynamic multipole polarizabilities $\alpha_{l, l'}^m(i\xi)$, which are defined and calculated in Sec. III, evaluated at imaginary frequencies. The coefficient specifying the isotropic part of the R^{-6} term reads

$$C(110; 110; 0) = \frac{1}{3\pi} \int_0^\infty \{\alpha_{11}^0(i\xi) + 2\alpha_{11}^1(i\xi)\}^2 d\xi.$$

The coefficients associated with the orientational dependent part of the R^{-6} term are given by^{1,5,11}

$$C(110; 112; 0) = \frac{1}{3\pi} \int_0^\infty \{\alpha_{11}^0(i\xi) + 2\alpha_{11}^1(i\xi)\} \{\alpha_{11}^0(i\xi) - \alpha_{11}^1(i\xi)\} d\xi,$$

$$C(112; 112; 0) = \frac{3}{2} C(112; 112; \pm 1) = 3C(112; 112; \pm 2) = \frac{1}{\pi} \int_0^\infty \{\alpha_{11}^0(i\xi) - \alpha_{11}^1(i\xi)\}^2 d\xi.$$

The R^{-8} 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

$$C(110; 220; 0) = \frac{1}{2\pi} \int_0^\infty \{\alpha_{11}^0(i\xi) + 2\alpha_{11}^1(i\xi)\} \{\alpha_{22}^0(i\xi) + 2\alpha_{22}^1(i\xi) + 2\alpha_{22}^2(i\xi)\} d\xi.$$

The orientational dependent part of the R^{-8} term that originates from the dipole-quadrupole interaction is specified by the following coefficients:

$$C(110; 222; 0) = \frac{4}{7\pi} \int_0^\infty \{\alpha_{11}^0(i\xi) + 2\alpha_{11}^1(i\xi)\} \{\alpha_{22}^0(i\xi) + \alpha_{22}^1(i\xi) - 2\alpha_{22}^2(i\xi)\} d\xi,$$

$$C(110; 224; 0) = \frac{1}{7\pi} \int_0^\infty \{\alpha_{11}^0(i\xi) + 2\alpha_{11}^1(i\xi)\} \{3\alpha_{22}^0(i\xi) - 4\alpha_{22}^1(i\xi) + \alpha_{22}^2(i\xi)\} d\xi,$$

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$$C(112; 220; 0) = \frac{2}{5\pi} \int_0^\infty \{ \alpha_{11}^0(i\xi) - \alpha_{11}^1(i\xi) \} \{ \alpha_{22}^0(i\xi) + 2\alpha_{22}^1(i\xi) + 2\alpha_{22}^2(i\xi) \} d\xi,$$

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

$$C(112; 224; 0) = \frac{22}{3\sqrt{30}} C(112; 224; \pm 1) = \frac{11}{\sqrt{15}} C(112; 224; \pm 2) = \frac{22}{35\pi} \int_0^\infty \{ \alpha_{11}^0(i\xi) - \alpha_{11}^1(i\xi) \} \{ 3\alpha_{22}^0(i\xi) - 4\alpha_{22}^1(i\xi) + \alpha_{22}^2(i\xi) \} d\xi.$$

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

$$C(110; 132; 0) = \frac{6}{7\pi} \int_0^\infty \{ \alpha_{11}^0(i\xi) + 2\alpha_{11}^1(i\xi) \} \left\{ \alpha_{13}^0(i\xi) + \frac{2\sqrt{6}}{3} \alpha_{13}^1(i\xi) \right\} d\xi,$$

$$C(110; 134; 0) = \frac{10}{21\pi} \int_0^\infty \{ \alpha_{11}^0(i\xi) + 2\alpha_{11}^1(i\xi) \} \left\{ \alpha_{13}^0(i\xi) - \frac{\sqrt{6}}{2} \alpha_{13}^1(i\xi) \right\} d\xi,$$

$$C(112; 132; 0) = 3C(112; 132; \pm 1) = -6C(112; 132; \pm 2) = \frac{6}{7\pi} \int_0^\infty \{ \alpha_{11}^0(i\xi) - \alpha_{11}^1(i\xi) \} \left\{ \alpha_{13}^0(i\xi) + \frac{2\sqrt{6}}{3} \alpha_{13}^1(i\xi) \right\} d\xi,$$

$$C(112; 134; 0) = \frac{38}{5\sqrt{30}} C(112; 134; \pm 1) = \frac{38}{3\sqrt{15}} C(112; 134; \pm 2) = \frac{38}{21\pi} \int_0^\infty \{ \alpha_{11}^0(i\xi) - \alpha_{11}^1(i\xi) \} \left\{ \alpha_{13}^0(i\xi) - \frac{\sqrt{6}}{2} \alpha_{13}^1(i\xi) \right\} d\xi.$$

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

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

$$V(t) = - \sum_{l,m \geq 0} (f_{lm} Q_{lm}^* e^{i\omega t} + f_{lm}^* Q_{lm} e^{-i\omega t}). \quad (2)$$

The multipole operator Q_{lm} is defined as

$$Q_{lm} = + \sqrt{\frac{4}{2l+1}} \sum_{i=1}^N r_i^l Y_{lm}(\theta_i, \varphi_i),$$

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

$$\langle \bar{Q}_{lm} \rangle = \sum_{l'} \alpha_{ll'}^m(\omega) f_{l'm} e^{i\omega t}. \quad (3)$$

Here $\langle \dots \rangle$ indicates an expectation value with respect to the perturbed wave function and

$$\bar{Q}_{lm} = Q_{lm} - \langle Q_{lm} \rangle_0,$$

where $\langle Q_{lm} \rangle_0$ is the expectation value of Q_{lm} in the unperturbed state. The dynamic multipole polarizabilities can be calculated from¹²

$$\alpha_{ll'}^m(\omega) = \langle \psi_0 | \bar{Q}_{lm} | \chi_{l'm}(\omega) + \chi_{l'm}(-\omega) \rangle, \quad (4)$$

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

$$(H_0 - E_0 + \omega) \chi_{l'm}(\omega) - \bar{Q}_{l'm}^* \psi_0 = 0. \quad (5)$$

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

$$\alpha_{ll'}^m(\omega) = \sum_{\nu} \frac{(f_{ll'}^m)_{\nu 0}}{\omega_{\nu 0}^2 - \omega^2}, \quad (6)$$

where the oscillator strength $(f_{ll'}^m)_{\nu 0}$ is given by

$$(f_{ll'}^m)_{\nu 0} = 2\omega_{\nu 0} \langle \psi_0 | Q_{lm} | \psi_{\nu} \rangle \langle \psi_{\nu} | Q_{l'm}^* | \psi_0 \rangle. \quad (7)$$

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

$$L[\chi_{l'm}(\omega)] = \langle \chi_{l'm}(\omega) | (H_0 - E_0 + \omega) | \chi_{l'm}(\omega) \rangle - \langle \chi_{l'm}(\omega) | \bar{Q}_{l'm}^* | \psi_0 \rangle - \langle \psi_0 | \bar{Q}_{l'm} | \chi_{l'm}(\omega) \rangle, \quad (8)$$

with respect to variations of $\chi_{l'm}(\omega)$.

Following Kirkwood⁹ we choose a trial function of the form

$$\chi_{l'm}(\omega) = \sum_{l''} C_{l''l'}^m(\omega) \bar{Q}_{l''m}^* \psi_0, \quad (9)$$

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

$$C_{l''l'}^m(\omega) = [\mathbf{N}^{-1} \mathbf{M} + \omega \mathbf{I}]_{l''l'}^{-1}, \quad (10)$$

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

$$M_{l''l'}^m = \langle \psi_0 | \bar{Q}_{l''m} (H_0 - E_0) \bar{Q}_{l'm}^* | \psi_0 \rangle + \langle \psi_0 | \bar{Q}_{l'm} (H_0 - E_0) \bar{Q}_{l''m}^* | \psi_0 \rangle \\ = \langle \psi_0 | \sum_{i=1}^N (\text{grad}_i \bar{Q}_{l''m}) (\text{grad}_i \bar{Q}_{l'm}^*) | \psi_0 \rangle, \quad (11)$$

$$N_{l''l'}^m = 2 \langle \psi_0 | \bar{Q}_{l''m} \bar{Q}_{l'm}^* | \psi_0 \rangle. \quad (12)$$

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

$$\alpha_{ll'}^m(\omega) = \frac{1}{2} [\mathbf{N}(\mathbf{C}(\omega) + \mathbf{C}(-\omega))]_{ll'}. \quad (13)$$

Using elementary matrix theory¹³ one can write the dynamic multipole polarizabilities given by Eq. (13) in the form

TABLE I. Strength factors and effective excitation energies for $\alpha_{II'}^m(\omega)$ (in a. u.).

		Z_1	Δ_1	Z_2	Δ_2
H ₂	α_{11}^0	1.995	0.5977	0.005	1.048
	α_{11}^1	1.999	0.7430	0.001	1.050
	α_{22}^0	10.94	0.8847
	α_{22}^1	10.40	0.9027
	α_{22}^2	8.780	0.9344
	α_{13}^0	0.9708	0.5977	0.6518	1.048
	α_{13}^1	0.9820	0.7430	0.3429	1.050
	N ₂	α_{11}^0	8.224	0.8251	5.776
α_{11}^1		0.312	1.084	13.69	1.307
α_{22}^0		109.6	1.257
α_{22}^1		93.77	1.147
α_{22}^2		46.17	1.142
α_{13}^0		-25.80	0.8251	73.39	1.166
α_{13}^1		16.37	1.084	22.49	1.307

$$\alpha_{II'}^m(\omega) = \sum_{\mu} \frac{(Z_{II'}^m)_{\mu}}{(\Delta_{II'}^m)_{\mu}^2 - \omega^2} \quad (14)$$

Here the strength factors are given by

$$(Z_{II'}^m)_{\mu} = (\Delta_{II'}^m)_{\mu} [\mathbf{NR}^{(\mu)}]_{II'} \quad (15)$$

where $(\Delta_{II'}^m)_{\mu}$ are the eigenvalues of $\mathbf{N}^{-1}\mathbf{M}$ and $\mathbf{R}^{(\mu)}$ the corresponding residue matrices. Although of course approximations, the variationally determined dynamic polarizabilities satisfy the sum rules $S_{II'}^m(0)$ and $S_{II'}^m(-1)$. Indeed

TABLE II. Static multipole polarizabilities for H₂ and N₂ (in a. u.).

		Present work	Mulder <i>et al.</i> ^a	Meyer ^b
H ₂	α_{11}^0	5.59	7.33	6.441
	α_{11}^1	3.62	4.93	4.570
	α_{22}^0	14.0	17.99	17.78
	α_{22}^1	12.8	17.13	16.97
	α_{22}^2	10.1	14.33	13.85
	α_{13}^0	3.31	3.93	...
	α_{13}^1	2.09	2.88	...
N ₂	α_{11}^0	16.3	15.7	
	α_{11}^1	8.28	8.76	
	α_{22}^0	69.4	64.7	
	α_{22}^1	71.3	66.0	
	α_{22}^2	35.4	28.2	
	α_{13}^0	16.1	22.0	
	α_{13}^1	27.1	27.2	

^aReferences 7 and 8.

^bReference 6.

TABLE III. Dispersion force coefficients (in a. u.).

	H ₂ ↔ H ₂	N ₂ ↔ N ₂
C(110; 110; 0)	9.28	97.8
C(110; 112; 0)	1.05	17.2
C(112; 112; 0)	0.399	10.3
C(110; 220; 0)	74.2	1310
C(110; 222; 0)	8.81	383
C(110; 224; 0)	0.262	-42.4
C(112; 220; 0)	6.38	183
C(112; 222; 0)	1.22	82.2
C(112; 224; 0)	0.139	-36.3
C(110; 132; 0)	12.9	531
C(110; 134; 0)	0.543	-48.7
C(112; 132; 0)	1.44	89.5
C(112; 134; 0)	0.266	-37.8

$$\sum_{\mu} (Z_{II'}^m)_{\mu} = \sum_{\nu} (f_{II'}^m)_{\nu 0} = M_{II'} \quad (16)$$

$$\sum_{\mu} \frac{(Z_{II'}^m)_{\mu}}{(\Delta_{II'}^m)_{\mu}} = \sum_{\nu} \frac{(f_{II'}^m)_{\nu 0}}{\omega_{\nu 0}} = N_{II'} \quad (17)$$

IV. RESULTS AND DISCUSSION

The simplicity of the variational procedure for the calculation of dynamic polarizabilities outlined in the previous section lies in the fact that the strength factors and effective excitation energies can be calculated using standard techniques from matrices the elements of which are moments of the ground state electron density. For the hydrogen molecule the required moments have been calculated from the accurate wave function obtained by Newell¹⁴ and for the nitrogen molecule an accurate SCF wave function was used for this purpose.¹⁵ In Table I we present the strength factors and effective excitation energies for the dynamic multipole polarizabilities for H₂ and N₂. In Table II we compare the static polarizabilities that follow from the data presented in Table I to the values obtained by Meyer⁶ and Mulder *et al.*^{7,8}

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 $C(l_a l_b^M; M)$ 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.*^{7,8} it is useful to write the dispersion interaction in the following form:

$$U_{\text{disp}} = - \sum_{n=6, 8, \dots} \frac{C_n}{R^n} \sum_{L_a L_b=0}^{\min(L_a, L_b)} \sum_{M=0} \gamma_n^{L_a L_b M} P_{L_a}^M(\cos \theta_a) \times P_{L_b}^M(\cos \theta_b) \cos[M(\phi_a - \phi_b)]$$

where $\gamma_n^{000} \equiv 1$. The isotropic interaction coefficients C_6 and C_8 are given by

$$C_6 = C(110; 110; 0) \quad ,$$

$$C_8 = 2C(110; 220; 0) \quad .$$

The dipole anisotropic parameters $\gamma_6^{L_a L_b M}$ can be written as

TABLE IV. Anisotropic dispersion interaction parameters.

	H ₂ ↔ H ₂			N ₂ ↔ N ₂	
	present work	Mulder <i>et al.</i> ^a	Meyer ^b	present work	Mulder ^c
γ_6^{200}	0.113	0.120	0.100	0.176	0.165
γ_6^{220}	0.043	0.044	0.031	0.106	0.087
$(\gamma_8^{200})_{\text{quadr}}$	0.102	0.091	0.089	0.216	0.230
$(\gamma_8^{200})_{\text{cross}}$	0.173	0.159	...	0.405	0.459
γ_8^{200}	0.276	0.250	...	0.621	0.689
$(\gamma_8^{220})_{\text{quadr}}$	0.016	0.013	0.0124	0.063	0.067
$(\gamma_8^{220})_{\text{cross}}$	0.039	0.038	...	0.137	0.148
γ_8^{220}	0.055	0.051	...	0.200	0.214
$(\gamma_8^{400})_{\text{quadr}}$	0.0018	-0.00051	0.0002	-0.016	-0.016
$(\gamma_8^{400})_{\text{cross}}$	0.0073	0.00514	...	-0.037	-0.030
γ_8^{400}	0.0091	0.0046	...	-0.053	-0.045
$(\gamma_8^{420})_{\text{quadr}}$	0.0009	-0.00025	-0.00003	-0.014	-0.012
$(\gamma_8^{420})_{\text{cross}}$	0.0036	0.00231	...	-0.029	-0.020
γ_8^{420}	0.0045	0.0021	...	-0.043	-0.032

^aReference 7.^bReference 6.^cReference 8.

$$\gamma_6^{200} = C(112; 110; 0)/C_6,$$

$$\gamma_6^{220} = -\frac{9}{2}\gamma_6^{221} = 36\gamma_6^{222} = C(112; 112; 0)/C_6.$$

The anisotropy factors $\gamma_8^{L_a L_b M}$ are the sum of the contribution of the dipole-quadrupole interaction (quadratic terms) and the contribution of the mixed dipole-dipole, dipole octupole interaction (cross terms)

$$\gamma_8^{L_a L_b M} = (\gamma_8^{L_a L_b M})_{\text{quadr}} + (\gamma_8^{L_a L_b M})_{\text{cross}}.$$

The quadratic terms can be written as

$$(\gamma_8^{200})_{\text{quadr}} = \{C(112; 220; 0) + C(110; 222; 0)\}/C_8,$$

$$\begin{aligned} (\gamma_8^{220})_{\text{quadr}} &= -5(\gamma_8^{221})_{\text{quadr}} \\ &= 20(\gamma_8^{222})_{\text{quadr}} = 2C(112; 222; 0)/C_8, \end{aligned}$$

$$(\gamma_8^{400})_{\text{quadr}} = C(110; 224; 0)/C_8,$$

$$\begin{aligned} (\gamma_8^{420})_{\text{quadr}} &= -\frac{22}{3}(\gamma_8^{421})_{\text{quadr}} \\ &= 132(\gamma_8^{422})_{\text{quadr}} = C(112; 224; 0)/C_8. \end{aligned}$$

The cross terms can be written as

$$(\gamma_8^{200})_{\text{cross}} = 2C(110; 132; 0)/C_8,$$

$$\begin{aligned} (\gamma_8^{220})_{\text{cross}} &= -9(\gamma_8^{221})_{\text{cross}} \\ &= -72(\gamma_8^{222})_{\text{cross}} = 4C(112; 132; 0)/C_8, \end{aligned}$$

$$(\gamma_8^{400})_{\text{cross}} = 2C(110; 134; 0)/C_8,$$

$$\begin{aligned} (\gamma_8^{420})_{\text{cross}} &= -\frac{38}{5}(\gamma_8^{421})_{\text{cross}} \\ &= 152(\gamma_8^{422})_{\text{cross}} = 2C(112; 134; 0)/C_8. \end{aligned}$$

In Table IV we present the anisotropy parameters

$\gamma_8^{L_a L_b M}$ ($n=6, 8$) and compare them with the results obtained by Meyer⁶ (who only calculated the quadratic terms) and Mulder *et al.*^{7, 8} We see that the overall agreement is indeed satisfactory except in the case of the $(\gamma_8^{400})_{\text{quadr}}$ and $(\gamma_8^{420})_{\text{quadr}}$ terms for the H₂ 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.

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