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New bounds for Van der Waals coefficients

R. Luyckx, F. Delbaen, Ph. Coulon, and H. N. W. Lekkerkerker
Faculteit van de Wetenschappen, Vrije Universiteit Brussel, 1050 Brussel, Belgium

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New upper and lower bounds for Van der Waals coefficients using even and odd oscillator-strength sum rules are derived.

About ten years ago Langhoff and Karplus[1-3] and Gordon[4] for the first time reported methods for determining upper and lower bounds for Van der Waals coefficients. These bounds were constructed by using in the Casimir-Polder integral formula[5] approximate dynamic polarizabilities that are upper or lower bounds to the exact dynamic polarizabilities at imaginary frequencies. These bounded dynamic polarizabilities were obtained by recognizing that the series expansion of $\alpha(i\xi)$ in positive powers of ξ^2 is a series of Stieltjes (the expansion coefficients being the even moments of the oscillator strength distribution) and subsequent use of results from the theory of Padé approximants[1-3] or Gaussian integration theory.[4] It has been shown that the two methods are equivalent.[6]

The fact that the above procedures only use even oscillator-strength sum rules was considered to be an advantage at the time since for the dipole case these sum rules can be obtained from optical refractivity data.[7] However, at the present time it becomes increasingly feasible to calculate both even and odd oscillator-strength sum rules rather accurately.[8] Further, for the calculation of higher-order dispersion forces the necessary experimental data are difficult to obtain and one has to resort to theoretical information anyway. So for these cases the even sum rules do not occupy a favored position. Therefore the question arises whether it is possible to construct bounds on the Van der Waals coefficients using both even and odd sum rules. An elegant method for doing this has been worked out by Alexander.[9] His procedure does not require the intermediate construction of an approximate polarizability and the upper and lower bounds are expressed directly in even and odd oscillator-strength sum rules and the smaller of the lowest excitation frequencies of the interacting species. However, the bounds provided by this method are not optimal. Further, Langhoff[10] has devised bounds on Van der Waals coefficients using the oscillator-strength sum rules $S(2), S(1), S(0), S(-1), S(-2)$ and the lowest resonance frequency ω_1.

In this paper we present a method rather similar in spirit to those of Langhoff and Karplus[1-3] and Gordon[4] to obtain bounds on the Van der Waals coefficients from both even and odd oscillator-strength sum rules. The starting point of our procedure is again the Casimir-Polder formula in which the dispersion interaction is expressed as an integral over imaginary frequencies of the appropriate dynamic polarizabilities of the interacting species. For example, the Van der Waals coefficient for the leading term of the dispersion interaction between two spherically symmetric atoms A and B,

$$u_{AB}=-C_{AB}/R^6\,,$$

can be written

$$C_{AB}=\frac{3}{\pi}\int_0^\infty \alpha_A(i\xi)\alpha_B(i\xi)\,d\xi\,. \tag{1}$$

Here $\alpha(i\xi)$ is the dynamic dipole polarizability

$$\alpha(i\xi)=\int_0^\infty \frac{d\psi(u)}{u^2+\xi^2}\,, \tag{2}$$

where $d\psi(u)$ is the oscillator-strength density between u and $u+du$. Substituting the dynamic polarizability given by (2) in (1), one obtains

$$C_{AB}=\frac{3}{2}\int_0^\infty d\psi_A(u)\int_0^\infty d\psi_B(v)\frac{1}{uv(u+v)}\,. \tag{3}$$

We now construct an approximate oscillator-strength distribution

$$d\bar{\psi}(u)=\sum_{i=1}^{n}\bar{f}_i\,\delta(u-\bar{u}_i)\,du\,, \tag{4}$$

where the weights $\bar{f}_i$ and positions $\bar{u}_i$ are determined by the condition that $d\bar{\psi}(u)$ reproduces $2n$ oscillator-strength sum rules

$$\int_0^\infty d\bar{\psi}(u)u^k=\int_0^\infty d\psi(u)u^k=S(k)\,,$$

$$k=-q,\ -q-1,\ \ldots,\ -q-2n+1, \tag{5}$$

where[11] $q=-2,-1,0,1,2,3,\ldots$ and $n=1,2,3,\ldots$

From the results mentioned in Ref. 12 it follows that this problem has a solution with all $\bar{f}_i$ and $\bar{u}_i$ real and positive. At this point we would like to emphasize that the approximate polarizabilities $\alpha(i\xi)$ that one obtains by substituting $d\bar{\psi}(u)$ in (2) are neither upper nor lower bounds to the exact polarizability at imaginary frequencies. Still it is possible to show that the approximate Van der Waals coefficients

$$\bar{C}_{AB}=\frac{3}{2}\int_0^\infty d\bar{\psi}_A(u)\int_0^\infty d\bar{\psi}_B(v)\,\frac{1}{uv(u+v)} \qquad (6)$$

are upper and lower bounds depending on which sum rules are used for the construction of the approximate oscillator-strength densities. Indeed the approximate oscillator-strength densities can be divided into two groups, where group I comprises the cases $q=-2,0,2,3,4,\ldots,n=1,2,3,\ldots$ and $q=-1,n=1$ and group II the remaining cases $q=-1,n=2,3,4,\ldots$ and $q=1,n=1,2.3,4,\ldots$, such that the Van der Waals coefficients calculated with approximate oscillator-strength densities that belong to group I are lower bounds, whereas those calculated with group II are upper bounds. The way we will demonstrate this is rather similar to the method Wheeler and Gordon[13] use to obtain bounds for averages using moments.

The upper bound obtained by Langhoff[10] using the oscillator-strength sum rules $S(1),S(0),S(-1)$, and $S(-2)$ is just a special case of group II, namely, $q=-1$ and $n=2$.

Introducing the variables $x=1/u$ and $y=1/v$ the approximate Van der Waals coefficients takes the form

$$\bar{C}_{AB}=\frac{3}{2}\int_0^\infty d\bar{\phi}_A(x)\int_0^\infty d\bar{\phi}_B(y)\,\frac{x^2y^2}{(x+y)}\,, \qquad (7)$$

where the approximate oscillator-strength densities now satisfy the relations

$$\int_0^\infty d\bar{\phi}(x)x^k=\int_0^\infty d\phi(x)x^k=S(-k)\,,$$

$$k=q,q+1,\ldots,q+2n-1 \qquad (8)$$

and places weight at the positions

$$\bar{x}_1=1/\bar{u}_1,\ \ \bar{x}_2=1/\bar{u}_2,\ldots,\bar{x}_n=1/\bar{u}_n\,.$$

It will appear that it is sufficient to show that for approximate oscillator-strength densities that belong to group I the following inequality holds:

$$\int_0^\infty d\phi(x)\,\frac{x^2}{x+a}\geqslant\int_0^\infty d\bar{\phi}(x)\,\frac{x^2}{x+a}\,,\quad a>0, \qquad (9)$$

and that for group II the opposite inequality applies. In order to prove (9) we consider the $(2n-1)$ degree Hermite interpolating polynomial $P_{2n-1,q}(x)$ for the function $F_q(x)=x^{(2-q)}/(x+a)$ which is constructed such that

$$P_{2n-1,q}(\bar{x}_i)=F_q(\bar{x}_i)\ ,\ P'_{2n-1,q}(\bar{x}_i)=F'_q(\bar{x}_i)$$

$$i=1,2,\ldots,n\,. \qquad (10)$$

It is well known[14] that

$$F_q(x)-P_{2n-1,q}(x)=\frac{1}{(2n)!}\prod_{i=1}^{n}(x-x_i)^2F_q^{(2n)}(\zeta), \qquad (11)$$

where if $x>0$, then $\zeta>0$.

A tedious but straightforward calculation shows that for q and n values belonging to group I $F_q^{(2n)}(\zeta)\geqslant 0$ for $\zeta>0$ and that for group II $F_q^{(2n)}(\zeta)\leqslant 0$ for $\zeta>0$.

In view of (11) this means that for group I

$$\int_0^\infty d\phi(x)\,\frac{x^2}{x+a}\geqslant\int_0^\infty d\phi(x)x^qP_{2n-1,q}(x)\,,\quad a>0 \qquad (12)$$

and that for group II the opposite inequality holds. For both groups the following equalities hold:

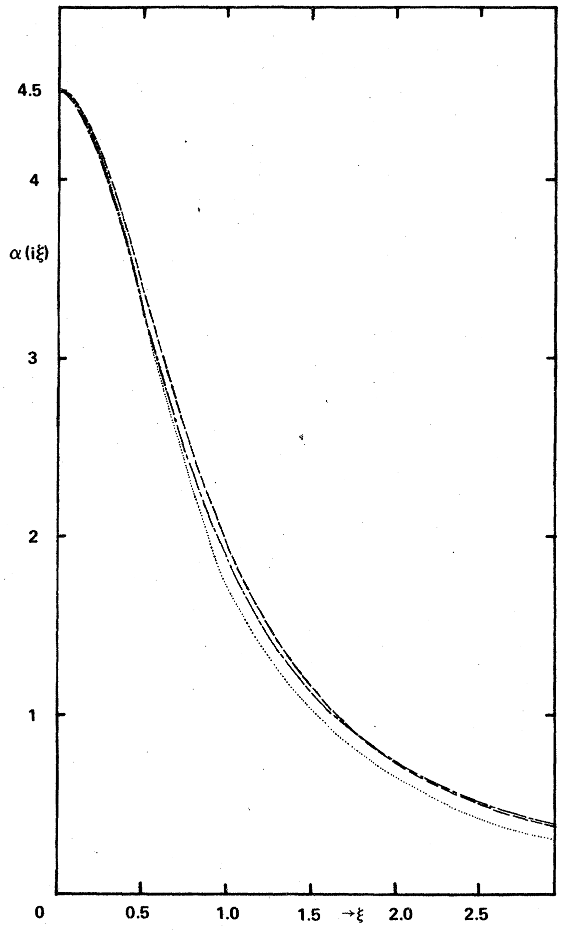

FIG. 1. Dynamic dipole polarizability for the hydrogen atom at imaginary frequencies. - •-, exact value [M. Karplus and H. J. Kolker, J. Chem. Phys. 39, 1493 (1963)]; ---, approximate dynamic polarizability that satisfies $S(-1)$ and $S(-2)$ (results in an upper bound for the Van der Waals coefficient); •••, approximate dynamic polarizability that satisfies $S(-2)$ and $S(-3)$ (results in a lower bound for the Van der Waals coefficient).

TABLE I. Dipole-dipole dispersion interaction coefficients between two hydrogen atoms.

	This work		Alexander (Ref. 9)		Langhoff and Karplus (Ref. 2)	
	Lower $q=2$	Upper $q=1$	Lower	Upper	Lower $[n,n-1]_\alpha$	Upper $[n,n-1]_\beta$
$n=1$	6.358	6.750	6.289	⋯	6.249	7.159
$n=2$	6.496	6.505	6.473	6.525	6.470	6.540
$n=3$	6.499	6.499	6.494	6.503	6.493	6.506

$$\int_0^\infty d\phi(x)x^q P_{2n-1,q}(x)=\int_0^\infty d\bar{\phi}(x)x^q P_{2n-1,q}(x)$$
$$=\int_0^\infty d\bar{\phi}(x)\,\frac{x^2}{x+a}\,,\quad a>0\,. \tag{13}$$

The first equality relies on the fact that the exact and approximate oscillator-strength densities have the same moments $S(-k), k=q,q+1,\ldots,q+2n-1$ and the second equality is due to the fact that at the n points $\bar{x}_1,\bar{x}_2,\ldots,\bar{x}_n$ where $d\bar{\phi}(x)$ places weight the function $x^q P_{2n-1,q}(x)$ and $x^2/(x+a)$ coincide. Combining (12) and (13) one obtains the result expressed by (9). Using this result together with Fubini's theorem on multiple integrals one can write for group I

$$\begin{aligned}
C_{AB}&=\tfrac{3}{2}\int_0^\infty d\phi_A(x)x^2\int_0^\infty d\phi_B(y)\,\frac{y^2}{x+y}\\
&\geqslant\tfrac{3}{2}\int_0^\infty d\phi_A(x)x^2\int_0^\infty d\bar{\phi}_B(y)\,\frac{y^2}{x+y}\\
&\geqslant\tfrac{3}{2}\int_0^\infty d\bar{\phi}_B(y)y^2\int_0^\infty d\phi_A(x)\,\frac{x^2}{x+y}\\
&\geqslant\tfrac{3}{2}\int_0^\infty d\bar{\phi}_B(y)y^2\int_0^\infty d\bar{\phi}_A(x)\,\frac{x^2}{x+y}\\
&\geqslant\bar{C}_{AB}\,.
\end{aligned}$$

Using the same kind of reasoning one obtains the opposite inequality for group II.

In Fig. 1 we illustrate that the approximate polarizabilities we use here to obtain bounds on the Van der Waals coefficients are themselves not upper or lower bounds for the exact polarizability at imaginary frequencies. This figure should be compared to Fig. 1 of Ref. 2.

In Table I we present some results for the dipole-dipole Van der Waals coefficient between hydrogen atoms. The first column gives the lower bounds obtained using dynamic polarizabilities that satisfy the sum rules $S(-2),S(-3),\ldots,S(-1-2n)$ and the second column gives the upper bounds obtained by using dynamic polarizabilities that satisfy the sum rules $S(-1),S(-2),\ldots,S(-2n)$. For the sake of comparison we have added bounds obtained by Alexander[9] using exactly the same sum rules as we do and in addition the lowest excitation energy. Further, we have also included in Table I the lower and upper bounds provided by the Padé approximants $[n,n-1]_\alpha$ and $[n,n-1]_\beta$ introduced by Langhoff and Karplus.[2] The $[n,n-1]_\alpha$ approximant reproduces the $2n$ even sum rules $S(-2)$, $S(4),\ldots,S(-4n)$ and the $[n,n-1]_\beta$ approximant reproduces the $2n$ even sum rules $S(0),S(-2),\ldots,S(-4n+2)$. From this table we conclude that the convergence of the bounding procedures presented here is quite good.

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