PHYSICAL REVIEW VOLUME 177, NUMBER 1 5 JANUARY 1969

# Dynamic Polarizabilities and van der Waals Coefficients*

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(Received 2 August 1968)

A simple two-point Padé approximant of the dynamic polarizability is used to generate a variety of formulas for van der Waals coefficients including the Slater-Kirkwood formula for two-body interactions and the Midzuno-Kihara formula for three-body interactions. The mathematical properties of the approximant are examined. It is shown that some formulae are bounds of the actual value while others give remarkably accurate results.

## 1. INTRODUCTION

The long-range interaction (van der Waals force) has long been recognized as a problem of major interest in the fields of interatomic forces. The two-body interactions were first formulated by Eisenshitz and London[1] who used a second-order perturbation sum over all excited states. The three-body interactions were first studied with the third-order perturbation method by Muto[2] and by Axilrod and Teller.[3] These problems were also approached by variational methods.[4,5] Whatever the approach, *ab initio* calculation is often tedious and requires the use of many-parameter wave functions.[6,7]

More recently, attention has been given to an alternate, though closely related, expression for the van der Waals coefficients in terms of an integral over imaginary frequency of products of the dynamic polarizabilities of the interacting atoms.[6,8] Since the required one-dimensional integration is straightforward, this approach reduces the original many-center problem to one of evaluating the dynamic polarizability of a single atom.

To use the integral formulation, a suitable analytic form for the dynamic polarizability is needed because the limit of integration goes to infinity and the frequency extends to the imaginary domain. To construct such an analytic expression, the Padé approximant method has been presented,[9] and proper bounds of each successive order of approximation has been established.[10]

In the process of these developments, many simple approximate formulae for van der Waals coefficients are derived such as the Slater-Kirkwood formula[4] for two-body interactions and the Midjuno-Kihara formula[5] for three-body interactions. They become well known because they are in closed forms and can provide a quick estimate for various interactions. In this paper, we shall use a simple two-point Padé approximant[11] of the dynamical polarizability to summarize these well-known formulae as well as to generate new ones. In certain cases this gives new meaning to the approximate formulae while in others this facilitates the establishment of bounds of the actual value.

In Sec. 2 we outline the method; in Sec. 3 a mathematical study of that simple approximant is made; in Sec. 4 we discuss the properties of various formulae derived.

## 2. THEORY OF DISPERSION ENERGY

From the perturbation theory, the van der Waals energy $E_{AB}$ for the interaction of two ground-state spherically symmetric atoms $A$ and $B$ is [1] (in atomic units)

$$E_{AB} = -C_{AB} R_{AB}^{-6}$$

with

$$C_{AB} = \tfrac{3}{2} \sum_l \sum_m f_l^A f_m^B / \epsilon_l^A \epsilon_m^B (\epsilon_l^A + \epsilon_m^B), \quad (2.1)$$

where $l$ and $m$ represent the quantum numbers of the excited states of atoms $A$ and $B$; $\epsilon_l^A$ and $\epsilon_m^B$ are the corresponding excitation energies; and $f_l^A$ and $f_m^B$ are the dipole oscillator strengths for excitation from the ground states of atoms $A$ and $B$. It is understood throughout the paper that the summation includes the integration over the continuum. The same theory, applied to the long-range interactions between three spherically symmetric atoms $A$, $B$, and $C$, yields the energy expression[3]

$$E_{ABC} = E_{AB} + E_{BC} + E_{CA} + \frac{D_{ABC}(3\cos\theta_A \cos\theta_B \cos\theta_C + 1)}{(R_{AB} R_{BC} R_{CA})^3}$$

with

$$D_{ABC} = \frac{3}{2} \sum_l \sum_m \sum_n \frac{f_l^A f_m^B f_n^C}{\epsilon_l^A \epsilon_m^B \epsilon_n^C} \times \frac{\epsilon_l^A + \epsilon_m^B + \epsilon_n^C}{(\epsilon_l^A + \epsilon_m^B)(\epsilon_m^B + \epsilon_n^C)(\epsilon_n^C + \epsilon_l^A)}, \quad (2.2)$$

where $\theta_A$, $\theta_B$, and $\theta_C$ are the internal angles of the triangle $ABC$; the definitions of other symbols correspond to those in Eq. (2.1).

Alternatively, the van der Waals energy can be expressed in terms of an integral over imaginary frequency of the product of the dynamic polarizabilities of the interacting species. The interactions between two atoms can be written as[12]

$$C_{AB} = (3/\pi) \int_0^\infty \alpha_A(i\omega) \alpha_B(i\omega) d\omega \quad (2.3)$$

and the non-additive contribution to the interactions between three atoms as[13]

$$D_{ABC}=(3/\pi)\int_0^{\infty}\alpha_A(i\omega)\alpha_B(i\omega)\alpha_C(i\omega)d\omega, \tag{2.4}$$

where $\alpha_A$, $\alpha_B$, and $\alpha_C$ are the dynamic polarizabilities of atoms $A$, $B$, and $C$, respectively. They are given by

$$\alpha_A(\omega)=\sum_{n=1}^{\infty}\frac{f_n^A}{(\epsilon_n^A)^2-\omega^2} \tag{2.5}$$

and the corresponding expressions for $\alpha_B(\omega)$ and $\alpha_C(\omega)$.

The equivalence of Eqs. (2.1) and (2.3) can be shown by means of the definite integral

$$\frac{2}{\pi}\int_0^{\infty}\frac{ab}{(a^2+x^2)(b^2+x^2)}dx=\frac{1}{a+b}\,. \tag{2.6}$$

Similarly the integral

$$\frac{2}{\pi}\int_0^{\infty}\frac{abc}{(a^2+x^2)(b^2+x^2)(c^2+x^2)}dx$$

$$=(a+b+c)/(a+b)(b+c)(c+a) \tag{2.7}$$

can be used to equate Eqs. (2.2) and (2.4).

It has been shown that the Padé approximant can be effectively used to evaluate $\alpha(i\omega)$.[9] Essentially it telescopes the infinite series into finite terms. The simplest approximation is the one-term formula

$$\alpha_A^{a}(\omega)=\alpha_A^{0}/[1-(\omega/\eta_A)^2], \tag{2.8}$$

where $\alpha_A^0$ is the static polarizability of atom $A$ and is given by

$$\alpha_A^0=\sum_{n=1}^{\infty}\frac{f_n^A}{(\epsilon_n^A)^2}\,. \tag{2.9}$$

It is clear from Eqs. (2.5), (2.8), and (2.9) that

$$\alpha_A^0=\alpha_A(0)=\alpha_A^a(0).$$

Equation (2.8) is equivalent to the two-point zeroth-order Padé approximant.[11] The information at the origin has been explicitly utilized. Various approximate formulae for van der Waals coefficients correspond to various choices for the other point (the determination of the constant $\eta$).

Substituting $\alpha^a(\omega)$ of Eq. (2.8) for $\alpha(\omega)$ in Eq. (2.3) and using Eq. (2.6), we obtain the well-known London formula

$$C_{AB}=\tfrac{3}{2}[\eta_A\eta_B/(\eta_A+\eta_B)]\,\alpha_A^0\alpha_B^0 \tag{2.10}$$

which was originally derived from Eq. (2.1) by the Unsöld closure approximation.[14] The empirical constants $\eta_A$ and $\eta_B$ are interpreted as average excitation energies. Values ranging from first excitation energy to ionization energy have been suggested for them.

If we require that infinity $|\infty|$ be the other point at which $\alpha^a(\omega)$ and $\alpha(\omega)$ should be equal, we can make use of the sum rule of the oscillatory strength

$$N_A=\sum_{l}^{\infty}f_l^A, \tag{2.11}$$

where $N_A$ is the number of electrons of atom $A$. Putting $\alpha_A(\omega\to\infty)=\alpha_A{}^a(\omega\to\infty)$ and using Eq. (2.11), we find

$$\eta_A=(N_A/\alpha_A^0)^{1/2}. \tag{2.12}$$

(If it is assumed that only outermost subshell of electrons contribute to polarizability, then $N_A$ is the number of electrons in this outer subshell.[15]) Substituting Eq. (2.12) and a corresponding expression for $\eta_B$ into Eq. (2.10), we obtain the Slater-Kirkwood formula[4]

$$C_{AB}=\frac{3}{2}\frac{\alpha_A^0\alpha_B^0}{(\alpha_A^0/N_A)^{1/2}+(\alpha_B^0/N_B)^{1/2}}\,. \tag{2.13}$$

This was first derived from a variational method which was proved to be equivalent to the perturbation method.[16] Later it was also derived from the dynamical polarizability.[17]

If the two-body coefficients of the homonuclear interactions are accurately known, the intersection point of $\alpha^a(i\omega)$ and $\alpha(i\omega)$ can be so chosen that $\alpha^a(i\omega)$ overestimates $\alpha(i\omega)$ in certain ranges of $\omega$ and underestimates $\alpha(i\omega)$ in other parts of the spectrum with the net result that $\alpha^a(i\omega)$ when substituted into Eq. (2.3) yields the correct value. (See Fig. 1 and Sec. IV.) The constant $\eta$ can be easily determined for such cases. For two identical atoms, Eq. (2.10) becomes

$$C_{AA}=\tfrac{3}{4}\eta_A(\alpha_A^0)^2$$

or

$$\eta_A=\tfrac{4}{3}C_{AA}/(\alpha_A^0)^2\,. \tag{2.14}$$

From this and the corresponding expression for $\eta_B$, the two-body coefficients of heteronuclear interactions can be obtained by substituting them back into Eq. (2.10) which then becomes

$$C_{AB}=\frac{2\alpha_A^0\alpha_B^0C_{AA}C_{BB}}{(\alpha_A^0)^2C_{BB}+(\alpha_B^0)^2C_{AA}}\,. \tag{2.15}$$

This formula has not been explicitly given before but it was implied in the work of Wilson[18] who took $N_A$ and $N_B$ as adjustable constants in the Slater-Kirkwood formula.

The three-body interactions can be calculated in a similar way. Replacing $\alpha^a(i\omega)$ for $\alpha(i\omega)$ in Eq. (2.4) and using Eq. (2.7) to evaluate the integral, we obtain

$$D_{ABC}=\tfrac{3}{2}\alpha_A^0\alpha_B^0\alpha_C^0$$

$$\times\frac{\eta_A\eta_B\eta_C(\eta_A+\eta_B+\eta_C)}{(\eta_A+\eta_B)(\eta_B+\eta_C)(\eta_C+\eta_A)}\,. \tag{2.16}$$

If we interpret $\eta_A$, $\eta_B$, and $\eta_C$ as the average excitation energies of atoms $A$, $B$, and $C$, Eq. (2.16) can be regarded as the three-body London

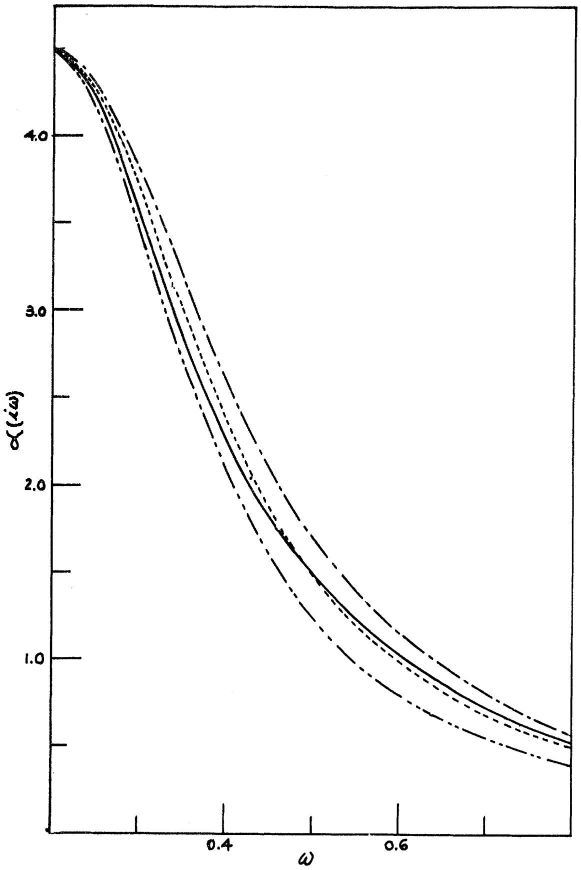

FIG. 1. The polarizability functions $\alpha(i\omega)$ of the hydrogen atom versus the frequency $\omega$. The solid curve gives the exact result; the – – – – curve is for $\eta$ equal to the first excitation energy; the —·—·— curve is for $\eta=(\alpha_H{}^0)^{-1/2}$; and the dashed curve is for $\eta=\frac{4}{3}C_{HH}\times(\alpha_H{}^0)^{-2}$.

formula. If Eq. (2.12) is used to determine $\eta_A$, $\eta_B$, and $\eta_C$, the result can be regarded as the generalized Slater-Kirkwood formula for three-body interactions. However, a much better approximation can be obtained if two-body coefficients are known. In that case, substituting Eq. (2.14) and corresponding expressions for $\eta_B$ and $\eta_C$ into Eq. (2.16), we obtain

$$D_{ABC}=\frac{2S_AS_BS_C(S_A+S_B+S_C)}{(S_A+S_B)(S_B+S_C)(S_C+S_A)} \tag{2.17}$$

with $\quad S_A=C_{AA}\alpha_B{}^0\alpha_C{}^0/\alpha_A{}^0$

and similar expressions for $S_B$ and $S_C$. For three identical atoms, Eq. (2.17) reduces to the Midzuno-Kihara formula[5]

$$D_{AAA}=\tfrac{3}{4}\alpha_A{}^0C_{AA}\,. \tag{2.18}$$

This equation can be obtained from the work of Muto[2] and of Axilrod,[19] using certain particular atomic models. Midzuno and Kihara obtained this equation by both the perturbation theory and the variational method.[5]

Equation (2.16) can be expressed in still another form. In Eq. (2.10) $C_{AB}$ is expressed in terms of $\eta_A$ and $\eta_B$. With two similar equations for $C_{BC}$ and $C_{AC}$' we have three simultaneous equations which can be solved for $\eta_A$', $\eta_B$, and $\eta_C$. Substituting these values into Eq. (2.16) and rearranging them, we obtain

$$D_{ABC}=\frac{2Q_AQ_BQ_C(Q_A+Q_B+Q_C)}{(Q_A+Q_B)(Q_B+Q_C)(Q_C+Q_A)} \tag{2.19}$$

with $\quad \dfrac{1}{Q_A}=\dfrac{1}{C_{AB}\alpha_C{}^0}+\dfrac{1}{C_{AC}\alpha_B{}^0}-\dfrac{1}{C_{BC}\alpha_A{}^0}$

and two corresponding expressions for $Q_B$ and $Q_C$. This equation was also given by Midzuno and Kihara who obtained it from a variational calculation with a particular type of trial function.[5]

The coefficient $D_{ABC}$ can be expressed in terms of $D_{AAA}$, $D_{BBB}$, and $D_{CCC}$. For three identical atoms, Eq. (2.16) becomes

$$D_{AAA}=\tfrac{9}{16}\eta_A(\alpha_A{}^0)^3.$$

Thus we have

$$\eta_A=\tfrac{16}{9}D_{AAA}/(\alpha_A{}^0)^3.$$

An identical expression is obtained when we combine Eqs. (2.14) and (2.18). The expressions for $\eta_B$ and $\eta_C$ can be obtained similarly. Substituting $\eta_A$, $\eta_B$, and $\eta_C$ back into Eq. (2.16), we obtain

$$D_{ABC}=\frac{8}{3}\,\frac{P_AP_BP_C(P_A+P_B+P_C)}{(P_A+P_B)(P_B+P_C)(P_C+P_A)} \tag{2.20}$$

with $\quad P_A=D_{AAA}\alpha_B{}^0\alpha_C{}^0/(\alpha_A{}^0)^2$

and two corresponding expressions for $P_B$ and $P_C$.

While some formulae derived in this section have been given before, others are new. The point we wish to emphasize here is that we can obtain these formulae very easily from a one-term approximation of the dynamic polarizability.

The three-body formulae are of special interest since far less is known in that case as compared with the two-body interactions. In view of our interpretation of the approximant, Eqs. (2.17)–(2.20) are probably more accurate than generally recognized. (See Sec. IV.)

### 3. RELATIONS BETWEEN $\alpha^a(i\omega)$ AND $\alpha(i\omega)$

Since we are concerned with the dynamic polarizability of only one single atom, the superscripts and subscripts identifying different atoms will be dropped in this section.

Let us consider the difference function between $\alpha^a(i\omega)$ and $\alpha(i\omega)$ as

$$g(\omega)=\alpha^a(i\omega)-\alpha(i\omega).$$

Using Eqs. (2.5), (2.8), and (2.9), we find

$$g(\omega)=\frac{\omega^2}{\eta^2+\omega^2}\sum_n\frac{(\eta^2-\epsilon_n^{\,2})f_n}{\epsilon_n^{\,2}(\epsilon_n^{\,2}+\omega^2)}\;. \tag{3.1}$$

If $\alpha^a(i\omega)$ and $\alpha(i\omega)$ are equal at the point $\omega_0$, then from Eq. (3.1) we have

$$\sum_n\frac{(\eta^2-\epsilon_n^{\,2})f_n}{\epsilon_n^{\,2}(\epsilon_n^{\,2}+\omega_0^{\,2})}=0\,. \tag{3.2}$$

For Eq. (3.2) to hold, there must exist a $k$ such that

$$\eta-\epsilon_k>0,\quad\text{and}\quad \eta-\epsilon_{k+1}<0.$$

Thus Eq. (3.2) can be written as

$$\sum_{n=1}^{k}\frac{(\eta^2-\epsilon_n^{\,2})f_n}{\epsilon_n^{\,2}(\epsilon_n^{\,2}+\omega_0^{\,2})}=\sum_{m=k+1}\frac{|\eta^2-\epsilon_m^{\,2}|f_m}{\epsilon_m^{\,2}(\epsilon_m^{\,2}+\omega_0^{\,2})}\,. \tag{3.3}$$

The derivative of the difference function at $\omega=\omega_0$ is

$$\begin{aligned}\left.\frac{dg(\omega)}{d\omega}\right|_{\omega=\omega_0}&=-2\frac{\omega_0^{\,3}}{\eta^2+\omega_0^{\,2}}\sum_n\frac{(\eta^2-\epsilon_n^{\,2})f_n}{\epsilon_n^{\,2}(\epsilon_n^{\,2}+\omega_0^{\,2})^2}\\&=-2\frac{\omega_0^{\,3}}{\eta^2+\omega_0^{\,2}}\left(\sum_{n=1}^{k}\frac{(\eta^2-\epsilon_n^{\,2})f_n}{\epsilon_n^{\,2}(\epsilon_n^{\,2}+\omega_0^{\,2})^2}\right.\\&\qquad\left.-\sum_{m=k+1}\frac{|\eta^2-\epsilon_m^{\,2}|f_m}{\epsilon_m^{\,2}(\epsilon_m^{\,2}+\omega_0^{\,2})^2}\right)\,.\end{aligned} \tag{3.4}$$

Since $\epsilon_k\geqslant\epsilon_n$ for $n=1,2\cdots k$, it follows that

$$\sum_{n=1}^{k}\frac{(\eta^2-\epsilon_n^{\,2})f_n}{\epsilon_n^{\,2}(\epsilon_n^{\,2}+\omega_0^{\,2})^2}>\frac{1}{\epsilon_k^{\,2}+\omega_0^{\,2}}\sum_{n=1}^{k}\frac{(\eta^2-\epsilon_n^{\,2})f_n}{\epsilon_n^{\,2}(\epsilon_n^{\,2}+\omega_0^{\,2})}\,. \tag{3.5}$$

Also because $\epsilon_k<\epsilon_m$ for $m=k+1,k+2\cdots$, we have

$$\sum_{m=k+1}\frac{|\eta^2-\epsilon_m^{\,2}|f_m}{\epsilon_m^{\,2}(\epsilon_m^{\,2}(\epsilon_m^{\,2}+\omega_0^{\,2})^2}<\frac{1}{\epsilon_k^{\,2}+\omega_0^{\,2}}\sum_{m=k+1}\frac{|\eta^2-\epsilon_m^{\,2}|f_m}{\epsilon_m^{\,2}(\epsilon_m^{\,2}+\omega_0^{\,2})}\,. \tag{3.6}$$

By Eq. (3.3), the right-hand sides of (3.5) and (3.6) are equal, therefore

$$\sum_{n=1}^{k}\frac{(\eta^2-\epsilon_n^{\,2})f_n}{\epsilon_n^{\,2}(\epsilon_n^{\,2}+\omega_0^{\,2})^2}>\sum_{m=k+1}\frac{|\eta^2-\epsilon_m^{\,2}|f_m}{\epsilon_m^{\,2}(\epsilon_m^{\,2}+\omega_0^{\,2})^2}\,. \tag{3.7}$$

Thus Eq. (3.4) shows that the derivative of $g(\omega)$ at $\omega=\omega_0$ is negative. This means

$$\begin{aligned}g(\omega)&>0,\quad\text{for}\quad\omega<\omega_0;\\&<0,\quad\text{for}\quad\omega>\omega_0.\end{aligned} \tag{3.8}$$

Let $\omega_1$ be the next root of $g(\omega)$; then by the above argument, we have in the neighborhood of $\omega_1$

$$\begin{aligned}g(\omega)&>0,\quad\text{for}\quad\omega<\omega_1\\&<0,\quad\text{for}\quad\omega>\omega_1.\end{aligned} \tag{3.9}$$

If $\omega_1>\omega_0$, then in the region between $\omega_0$ and $\omega_1$ we find $g(\omega)<0$ from (3.8), and $g(\omega)>0$ according to (3.9). Since this is impossible, we conclude that $g(\omega)$ has no root to the right of $\omega_0$. Similarly we can show that $g(\omega)$ has no nonzero root to the left of $\omega_0$. Hence we establish the following theorem.

> If $\alpha^a(i\omega)$ and $\alpha(i\omega)$ intersect at points other than the origin they intersect only once; that is, there exists only one $\omega_0$ such that $\alpha^a(i\omega_0)=\alpha(i\omega_0)$. Furthermore
>
> $$\alpha^a(i\omega)>\alpha(i\omega),\quad\text{for}\quad 0<\omega<\omega_0\,,$$
>
> $$\text{and}\quad\alpha^a(i\omega)<\alpha(i\omega),\quad\text{for}\quad\omega>\omega_0\,.$$

## 4. PROPERTIES OF APPROXIMATE FORMULAE

All the approximate formulae of van der Waals interactions presented in Sec. 2 are derived from the approximate dynamical polarizability $\alpha^a(i\omega)$ [Eq. (2.8)] which can be classified into three categories depending on the choice of $\eta$.

(1) $\alpha^a(i\omega)$ is everywhere greater than $\alpha(i\omega)$;
(2) $\alpha^a(i\omega)$ is everywhere smaller than $\alpha(i\omega)$;
(3) $\alpha^a(i\omega)$ and $\alpha(i\omega)$ intersect once.

These situations are illustrated in Fig. 1 for the interaction between two hydrogen atoms. Obviously, the van der Waals coefficients derived from the first category are upper bounds and that from the second category are lower bounds. Those in the third category should give fairly accurate results since $\alpha^a$ is so constructed that the part which overestimates $\alpha$ compensates the part which underestimates $\alpha$.

### (A) Two-body Interactions

If the parameter $\eta$ in the London formula [Eq. (2.10)] is taken to be the first excitation energy, then from Eq. (3.1) we see that the difference between $\alpha^a$ and $\alpha$ is always negative. Thus it is a lower bound. It is known that even with $\eta$ taken to be the ionization energy, the London formula still underestimates the van der Waals coefficients for most systems. This only shows that there are important contributions from the continuum part of the spectrum.

The Slater-Kirkwood formula corresponds to the fact that $\alpha^a(i\omega)$ and $\alpha(i\omega)$ exhibit the same behavior at infinity. Since they only intersect once and to the left of the intersection point $\alpha^a(i\omega)>\alpha(i\omega)$, then $\alpha^a(i\omega)$ is always an upper bound of $\alpha(i\omega)$ for any finite $\omega$.

The formula given by Eq. (2.15) belongs to the third category. It should be considerably more accurate than the "combining law,"[20]

$$C_{AB}=(C_{AA}C_{BB})^{1/2} \tag{4.1}$$

which is actually an upper bound.[21] In Table I, $C_{AB}$ calculated from Eq. (2.15) for some noble gases are presented. The results agree remarkably well with semi-empirical calculations.[22]

### (B) Three-body Interactions

As discussed in connection with Eq. (2.16), the generalized three-body London formula and three-body Slater-Kirkwood formula can be obtained in a straightforward way. They give lower and upper bounds corresponding to the two-body cases. However, Eqs. (2.17)–(2.20) give much closer approximations. They belong to the third category.

The Midzuno-Kihara formula [Eq. (2.18)] for three identical atoms has been shown to be a good approximation for hydrogen[23] and helium[9] atoms. In view of the present derivation, this ought to be true for all atoms. Furthermore, one can show that Eq. (2.18) is an upper bound of the coefficient. The difference between the approximated value and the exact value can be written as

$$\int_0^\infty \{[\alpha^a(i\omega)]^3 - [\alpha(i\omega)]^3\}d\omega$$

$$= \int_0^\infty [\alpha^a(i\omega) - \alpha(i\omega)][\alpha^a(i\omega)]^2 d\omega$$

$$+ \int_0^\infty \{[\alpha^a(i\omega)]^2 - [\alpha(i\omega)]^2\}\alpha(i\omega)d\omega. \qquad (4.2)$$

Since the parameter $\eta$ in $\alpha^a(i\omega)$ is so chosen that it yields the exact two-body coefficient, which means

$$\int_0^\infty \{[\alpha^a(i\omega)]^2 - [\alpha(i\omega)]^2\}d\omega = 0, \qquad (4.3)$$

it follows that (see Appendix A for proof)

$$\int_0^\infty [\alpha^a(i\omega) - \alpha(i\omega)]\alpha^a(i\omega)d\omega > 0. \qquad (4.4)$$

This relation together with the fact that $\alpha^a(i\omega)$ is monotone decreasing can be used to prove (see Appendix B)

$$\int_0^\infty [\alpha^a(i\omega) - \alpha(i\omega)][\alpha^a(i\omega)]^2 d\omega > 0. \qquad (4.5)$$

Similarly, because $\alpha(i\omega)$ is monotonically decreasing, one can use Eq. (4.3) to show that (see Appendix B)

$$\int_0^\infty \{[\alpha^a(i\omega)]^2 - [\alpha(i\omega)]^2\}\alpha(i\omega)d\omega > 0. \qquad (4.6)$$

Therefore from Eqs. (4.2), (4.5), and (4.6), we have

$$\int_0^\infty [\alpha^a(i\omega)]^3 d\omega > \int_0^\infty [\alpha(i\omega)]^3 d\omega. \qquad (4.7)$$

Some values of $D_{AAA}$ calculated from Eq. (2.18) are listed in Table II. As compared with the semi-empirical estimates, it is seen that Eq. (2.18) is indeed a very tight upper bound which overestimates only about three percent in all cases.

In Table III, some results from Eq. (2.20) are presented. They are almost identical with the semi-empirical estimates. This is a consequence of near proportionality of the dynamic polarizabilities of different atoms for all frequencies. This shows that if the three-body coefficients of homonuclear interactions are known exactly, Eq. (2.20) can be used to calculate $D_{ABC}$ to a high degree of accuracy. On the other hand, if only upper bounds of three identical atoms are known, the upper bound of three unlike atoms can be obtained from Eq. (2.20). If we substitute the values of $D_{AAA}$, $D_{BBB}$, and $D_{CCC}$ of Eq. (2.18) into Eq. (2.20), the expression obtained is identical with Eq. (2.17). Since Eq. (2.18) is an upper bound, we expect Eq. (2.17) to be an upper bound also. In Table IV, some coefficients for three unlike atoms calculated from Eq. (2.17) are listed. They are indeed upper bounds and, in general, only about three percent above the semi-empirical estimates.

The values calculated from Eq. (2.19), which is the Midzuno-Kihara formula for three unlike atoms, are also presented in Table IV. Their accuracy is slightly worse than that of Eq. (2.17). In addition, the equation is more difficult to calculate than Eq. (2.17). Therefore the latter is to be preferred.

TABLE I. Values of $C_{AB}$ in atomic units (1 a.u. $= e^2 a_0^5$).

| | | Semi-empirical estimates (Ref. 22) | This paper Eq. (2.15). $C_{AA}$ and $\alpha^0$ from Ref. 22 | Upper bound, Eq. (4.1). $C_{AA}$ from Ref. 22 |
|---|---|---|---|---|
| H | He | 2.81 | 2.80 | 3.07 |
| H | Ne | 5.62 | 5.65 | 6.40 |
| H | Ar | 19.93 | 19.96 | 20.60 |
| H | Kr | 28.53 | 28.62 | 29.10 |
| H | Xe | 41.61 | 41.66 | 41.76 |
| Ne | He | 3.01 | 3.02 | 3.03 |
| Ne | Ar | 19.60 | 19.64 | 20.29 |
| Ne | Kr | 27.26 | 27.22 | 28.67 |
| Ne | Xe | 37.49 | 37.41 | 41.13 |
| Ar | Kr | 92.10 | 92.04 | 92.35 |
| Ar | Xe | 130.35 | 130.09 | 132.35 |
| Kr | Xe | 185.70 | 185.70 | 186.99 |

TABLE II. Values of $D_{AAA}$ in atomic units (1 a.u. $= e^2 a_0^8$).

| | Semi-empirical estimate (Ref. 22) | Upper bound Eq. (2.18). $C_{AA}$ and $\alpha^0$ from Ref. 22 |
|---|---|---|
| H H H | 21.65 | 21.94 |
| He He He | 1.47 | 1.51 |
| Ne Ne Ne | 11.84 | 12.61 |
| Ar Ar Ar | 525.5 | 542.9 |
| Kr Kr Kr | 1578.5 | 1640.1 |
| Xe Xe Xe | 5285.0 | 5446.4 |

TABLE III. Values of $D_{ABC}$ in atomic units (1 a.u. $= e^2 a_0{}^8$).

| | Semi-empirical estimates (Ref. 22) | This paper Eq. (2.20) $D_{AAA}$ and $\alpha^0$ from Ref. 22 |
|---|---|---|
| H H He | 8.08 | 8.06 |
| H H Ne | 15.76 | 15.80 |
| H H Ar | 60.70 | 60.77 |
| H H Kr | 88.9 | 89.0 |
| H H Xe | 133.4 | 135.0 |
| H He He | 3.25 | 3.24 |
| H He Ne | 6.39 | 6.40 |
| H He Ar | 23.74 | 23.70 |
| H Ne Xe | 99.8 | 99.8 |
| H Ar Ar | 175.2 | 175.5 |
| He He Ne | 2.94 | 2.94 |
| He He Ar | 10.27 | 10.23 |
| He Ne Ne | 5.88 | 5.89 |
| He Ne Ar | 20.37 | 20.35 |
| Ne Ne Ar | 40.53 | 40.54 |
| Ne Ar Ar | 143.95 | 143.95 |
| Ne Ar Xe | 297.85 | 297.84 |
| Ar Ar Kr | 756.5 | 756.0 |
| Ar Kr Kr | 1091.5 | 1091.0 |
| Kr Xe Xe | 3508.5 | 3508.1 |

TABLE IV. Values of $D_{ABC}$ in atomic units (1 a.u. $= e^2 a_0{}^8$).

| | Semi-empirical estimates (Ref. 22) | This paper Eq. (2.17). $C_{AA}$ and $\alpha^0$ from Ref. 22 | Eq. (2.19). $C_{AB}$ and $\alpha^0$ from Ref. 22 |
|---|---|---|---|
| H He Xe | 51.1 | 51.99 | 52.09 |
| H Ne Ne | 12.60 | 13.08 | 13.01 |
| He He Kr | 14.60 | 14.95 | 15.03 |
| He He Xe | 21.02 | 21.38 | 21.55 |
| He Ne Kr | 28.91 | 29.95 | 30.04 |
| He Ne Xe | 41.47 | 42.64 | 42.84 |
| He Ar Ar | 72.95 | 74.95 | 75.09 |
| He Ar Kr | 104.4 | 107.35 | 107.70 |
| He Ar Xe | 152.1 | 155.67 | 156.40 |
| He Kr Kr | 149.8 | 154.26 | 154.84 |
| He Kr Xe | 219.35 | 224.95 | 225.93 |
| Ne Ne Kr | 57.4 | 60.14 | 60.21 |
| Ne Ne Xe | 82.0 | 85.18 | 85.34 |
| Ne Ar Kr | 205.7 | 213.89 | 213.93 |
| Ne Kr Kr | 294.6 | 306.68 | 306.94 |
| Ne Kr Xe | 430.4 | 445.57 | 446.01 |
| Ne Xe Xe | 634.5 | 654.26 | 654.97 |
| Ar Ar Xe | 1114.0 | 1148.0 | 1149.8 |
| Ar Kr Xe | 1614.5 | 1667.7 | 1669.1 |
| Ar Xe Xe | 2406.5 | 2479.1 | 2482.0 |

## APPENDIX A

If $$\int_0^\infty \{[\alpha^a(i\omega)]^2 - [\alpha(i\omega)]^2\} d\omega = 0, \tag{A.1}$$

then $$\int_0^\infty [\alpha^a(i\omega) - \alpha(i\omega)]\alpha^a(i\omega) d\omega > 0.$$

*Proof*: Since $\alpha^a(i\omega)$ and $\alpha(i\omega)$ are not identical, in order to satisfy Eq. (A.1), $\alpha^a(i\omega)$ and $\alpha(i\omega)$ have to intersect, but they intersect only once (see Sec. 2). If $\omega_0$ is the point of intersection,

$$\alpha(i\omega) < \alpha^a(i\omega), \quad \text{for} \quad \omega < \omega_0, \tag{A.2a}$$

and $$\alpha(i\omega) > \alpha^a(i\omega), \quad \text{for} \quad \omega > \omega_0. \tag{A.2b}$$

Equation (A.1) can be written as

$$\int_0^{\omega_0} [\alpha^a(i\omega) - \alpha(i\omega)][\alpha^a(i\omega) + \alpha(i\omega)] d\omega$$

$$- \int_{\omega_0}^\infty \alpha^a(i\omega) - \alpha(i\omega) \; [\alpha^a(i\omega) + \alpha(i\omega)] d\omega = 0. \tag{A.3}$$

Because of (A.2a),

$$2 \int_0^{\omega_0} [\alpha^a(i\omega) - \alpha(i\omega)]\alpha^a(i\omega) d\omega$$

$$> \int_0^{\omega_0} [\alpha^a(i\omega) - \alpha(i\omega)] \; [\alpha^a(i\omega) + \alpha(i\omega)] d\omega, \tag{A.4}$$

and because of (A.2b),

$$2 \int_{\omega_0}^\infty |\, \alpha^a(i\omega) - \alpha(i\omega) \,|\, \alpha^a(i\omega) d\omega$$

$$< \int_{\omega_0}^\infty |\, \alpha^a(i\omega) - \alpha(i\omega) \,|\, [\alpha^a(i\omega) + \alpha(i\omega)] d\omega. \tag{A.5}$$

Combining Eq. (A.3) and the inequalities (A.4) and (A.5), we find

$$2 \int_0^\infty [\alpha^a(i\omega) - \alpha(i\omega)]\,\alpha^a(i\omega) d\omega > 0.$$

Hence

$$\int_0^\infty [\alpha^a(i\omega) - \alpha(i\omega)]\alpha^a(i\omega) d\omega > 0. \tag{A.6}$$

## APPENDIX B

If $h(\omega)$ is positive and monotonically decreasing and $f(\omega)$ is such that

$$f(\omega) < 0, \quad \text{for} \quad \omega > \omega_0,$$
$$> 0, \quad \text{for} \quad \omega < \omega_0,$$

and $$\int_0^\infty f(\omega) d\omega \geqslant 0, \tag{B.1}$$

then $$\int_0^\infty f(\omega) h(\omega) d\omega > 0.$$

*Proof*:

$$\int_0^\infty f(\omega) h(\omega) d\omega$$

$$= \int_0^{\omega_0} f(\omega) h(\omega) d\omega - \int_{\omega_0}^\infty |f(\omega)|\, h(\omega) d\omega .$$

Since $h(\omega)$ is monotonically decreasing,

$$\int_0^{\omega_0} f(\omega) h(\omega) > h(\omega_0) \int_0^{\omega_0} f(\omega) d\omega \tag{B.2}$$

and

$$\int_{\omega_0}^{\infty} |f(\omega)|\, h(\omega) < h(\omega_0)\int_{\omega_0}^{\infty} |f(\omega)|\, d\omega\,. \tag{B.3}$$

Hence

$$\int_0^{\infty} f(\omega)h(\omega)d\omega > h(\omega_0)\int_0^{\infty} f(\omega)d\omega \geq 0. \tag{B.4}$$

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*Work supported in part by a grant from the Research Corporation.

[1] R. Eisenschitz and F. London, Z. Physik 60, 491 (1930).

[2] Y. Muto, Proc. Phys. Math. Soc. Japan 17, 629 (1943).

[3] B. M. Axilrod and E. Teller, J. Chem. Phys. 11, 299 (1943).

[4] J. C. Slater and J. G. Kirkwood, Phys. Rev. 37, 682 (1931).

[5] Y. Midzuno and T. Kihara, J. Phys. Soc. Japan 11, 1045 (1956).

[6] M. Karplus and H. J. Kolker, J. Chem. Phys. 41, 3955 (1964).

[7] W. D. Davison, Proc. Phys. Soc. (London) 87, 133 (1966).

[8] For recent reviews, see A. Dalgarno and W. D. Davison, Advan. At. Mol. Phys. 2, 1 (1966); A. Dalgarno, Advan. Chem. Phy. 12, 143 (1967).

[9] K. T. Tang and M. Karplus, Phys. Rev. 171, 70 (1968).

[10] P. W. Langhoff and M. Karplus, Phys. Rev. Letters 19, 1461 (1968).

[11] G. A. Baker, Advan. Theoret. Phys. 1, 1 (1965); G. A. Baker, G.S. Rushbrooke, and H.E. Gilbert, Phys. Rev. 135, A1272 (1964).

[12] H. B. G. Casimir and D. Polder, Phys. Rev. 73, 360 (1948); A. D. McLachlan, Proc. Roy. Soc. (London) A271, 387 (1963).

[13] A. D. McLachlan, Mol. Phys. 6, 423 (1963).

[14] F. London, Z. Physik. Chem. (Leipzig) B11, 222 (1930).

[15] L. Salem, Mol. Phys. 3, 441 (1960).

[16] A. Dalgarno and J. T. Lewis, Proc. Phys. Soc. (London) A69, 628 (1956).

[17] C. Mavroyannis and M. J. Stephens, Mol. Phys. 5, 629 (1962).

[18] J. N. Wilson, J. Chem. Phys. 43, 2564 (1965).

[19] B. M. Axilrod, J. Chem. Phys. 19, 724 (1951).

[20] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (John Wiley & Sons, Inc., New York, 1954), p. 963.

[21] K. T. Tang, J. Chem. Phys. 49, 4727 (1968).

[22] R. J. Bell and A. E. Kingston, Proc. Phys. Soc. (London) 88, 901 (1966).

[23] Y. M. Chan and A. Dalgarno, Mol. Phys. 9, 525 (1965).

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PHYSICAL REVIEW VOLUME 177, NUMBER 1 5 JANUARY 1969

# Doublet Suppression in the Principal Series of Cesium

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(Received 5 June 1968)

The suppression of the doublet structure in mixtures of cesium and foreign gases with increasing foreign gas concentration is investigated. The observations are made in absorption with the foreign gases helium, neon, argon, xenon, and neopentane. The foreign gases investigated which demonstrate complete suppression, xenon and neopentane, also produce satellites on both doublet components. The growth of the satellites with increasing foreign gas concentration is shown to produce anomalously broadened lines, considering that the satellite and its parent line together constitute the same transition. The anomalous broadening of the components results in excessive loss of measured absorption as the center of the lines is depressed and the absorption in the wings predominates. Assuming a minimum detectable absorptivity of 0.03, the absorption of the weaker components (${}^2P_{1/2}$) is seen to be undetectable for many of the higher doublets, while the strong components (${}^2P_{3/2}$) remain detectable, although considerably broadened.

## I. INTRODUCTION

Suppression of the doublet structure in the principal series of cesium was first observed in a satellite band study of mixtures of cesium and foreign gases in absorption.[1] More recently, the phenomenon has been observed in the emission spectrum of a cesium-xenon discharge.[2] The effect is evidenced by an apparent quenching of the ${}^2P_{1/2}$ components when the cesium vapor is in