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BOUNDS FOR van der WAALS COEFFICIENTS FROM PADÉ APPROXIMANTS*

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Recent refinements[1] in the experimental measurements of van der Waals (dispersion-force) interactions between neutral atoms have provided the stimulus for a concomitant development in theoretical techniques for their calculation.[2] In this Letter, we wish to report a method utilizing Padé approximants[3] for determining upper and lower bounds to van der Waals coefficients from theoretical and/or experimental values of the dynamic polarizability.

Restricting the discussion to the second-order, dipole-dipole coefficient C_{ab} ($E_{ab} = -C_{ab}/R^6$) for ground-state, spherically symmetric atoms a and b, we have from Casimir and Polder[4] that

$$C_{ab} = (3/\pi)\int_0^\infty \alpha_a(i\omega)\alpha_b(i\omega)d\omega, \tag{1}$$

where $\alpha_a(z)$ is the dynamic dipole polarizability of atom a,

$$\alpha_a(z) = \sum_{i=1}^{\infty} \frac{f_{ai}}{\omega_{ai}^2 - z^2} + \int_0^\infty \frac{[df_a(\epsilon)/d\epsilon]d\epsilon}{\omega_a(\epsilon)^2 - z^2} \tag{2}$$

and f_{ai}, ω_{ai} and $df_a(\epsilon)/d\epsilon$, $\omega_a(\epsilon)$ are the discrete and continuous oscillator strengths and transition frequencies, respectively. Expanding $\alpha_a(i\omega)$ in the form

$$\alpha_a(i\omega) = \sum_{k=0}^{\infty} \alpha_k(-\omega^2)^k, \tag{3}$$

with

$$\alpha_k = \sum_{i=1}^{\infty} \frac{f_{ai}}{\omega_{ai}^{2k+2}} + \int_0^\infty \frac{[df_a(\epsilon)/d\epsilon]d\epsilon}{[\omega_a(\epsilon)]^{2k+2}}, \tag{4}$$

we note that Eq. (3) is a series of Stieltjes.[3,5]

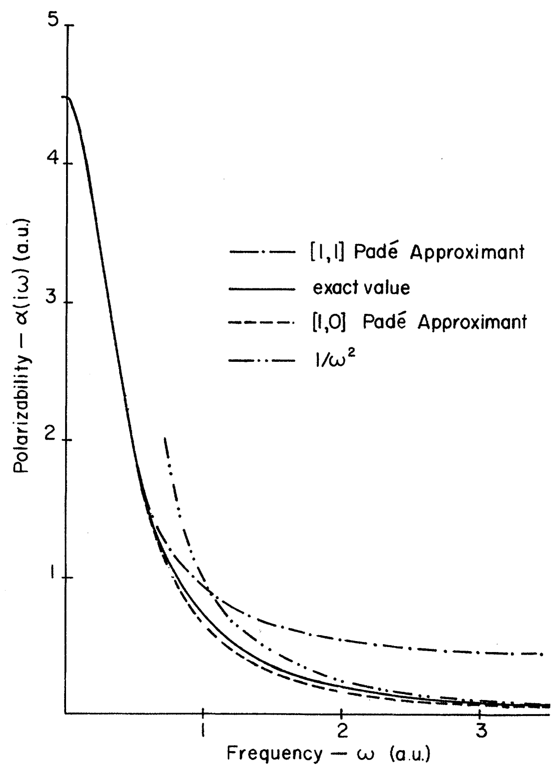

FIG. 1. Dipole polarizability $\alpha(i\omega)$ of atomic hydrogen as a function of ω.

Table I. Dipole coefficient C_{HH} (in a.u.) obtained from the $[n,n]$ and $[n,n-1]$ Padé approximants.[a]

n	Upper bound $[n,n]$	Lower bound $[n,n-1]$
1	6.780	6.249
2	6.542	6.470
3	6.517	6.493
4	6.499	6.497
5	6.499	6.498
6	6.499	6.499
7	6.499	6.499
Exact[a]	6.499	

[a]Value obtained by L. Pauling and J. Y. Beach, Phys. Rev. 47, 686 (1935); J. O. Hirschfelder and P. O. Löwdin, Mol. Phys. 2, 229 (1959), generally considered to be the exact nonrelativistic value for C_{HH}.

For positive ω^2, a continuation of this series which provides an upper and a lower bound, respectively, to the exact continuation is given by the $[n,n]$ and $[n,n-1]$ Padé approximants.[3] Use of these approximants to $\alpha_a(i\omega)$ and $\alpha_b(i\omega)$ in Eq. (1) yields the desired bounds for C_{ab}.

As an illustration of the method we have considered atomic hydrogen and calculated exact values for the α_k in Eq. (4). For the lowest-order Padé approximants [1, 1] and [1, 0], determined by the requirement that the power series expansion of these approximants equal Eq. (3) to order $k=2$ and $k=1$, respectively,[3] the results are compared with the exact values[6] for $\alpha_H(i\omega)$ in Fig. 1. Since the $[n,n]$ approximants approach a nonzero value as $i\omega\to\infty$ (see Fig. 1), a useful upper bound for $\alpha(i\omega)$ over the entire ω range is obtained by joining the $[n,n]$ approximant to the asymptotic limit $[\alpha_H(i\omega\to\infty)=N/\omega^2$, where N is the number of electrons], which is itself an upper bound, at the crossing point [Fig. 1]. Correspondingly, the upper-bound integral for C_{HH} [Eq. (1)] becomes a sum of two parts, the dividing ω value being determined by the crossing point of $[n,n]$ and N/ω^2. The resulting upper and lower bounds for C_{HH} are listed in Table I. Even the [1, 0] and [1, 1] bounds are within 5 % of the exact value and the [4, 4], [6, 5] results agree to four significant figures.

As an alternative to a purely theoretical approach, the required α_k values [Eq. (4)] can be obtained from optical-dispersion and related data, as well as from oscillator-strength sum rules. To illustrate this procedure, we use experimental estimates[7] for the first three α_k coefficients of the noble gases to construct the lowest-order Padé approximants and to determine semiempirical bounds for C_{ab}. The results are presented in Table II, which also includes experimental values, some of which fall outside the bounds (e.g., He-Ne, He-Ar). Tighter error bounds can be achieved with higher Padé approximants [see Table I] or by closely related methods[8] if additional data [e.g., excitation energies, oscillator strengths] are

Table II. Dipole coefficient C_{ab} coefficients (in a.u.) for some noble gases.

	Experiment	Lower bound [1, 0]	Upper bound [1, 1]	Average of bounds	Semiempirical estimates[f]
He-He	1.47[a]	1.37	1.59	1.48	1.47
He-Ne	4[b]	2.67	3.65	3.16	3.04
He-Ar	12,[b] 8.5[c]	8.82	11.64	10.23	9.65
Ne-Ne	6.3,[d] 6.4[d]	5.19	8.97	7.08	6.38
Ne-Ar	21[c]	17.15	27.14	22.14	19.7
Ar-Ar	61,[e] 63,[d] 67[d]	59.0	85.8	72.4	65.1

[a]Accurate calculation; e.g., Y. M. Chan and A. Dalgarno, Proc. Phys. Soc. (London) 86, 777 (1965); see, also, Ref. 2.

[b]From beam measured by R. Duren, R. Helbing, and H. Pauly, Z. Physik 188, 468 (1965).

[c]From beam measured by E. W. Rothe, L. L. Marino, R. H. Neynaber, P. U. Rol, and S. M. Trujillo, Phys. Rev. 126, 598 (1962); the values in the table are corrected from the original results as suggested by E. W. Rothe and R. H. Neynaber, J. Chem. Phys. 42, 3206 (1965).

[d]From low-temperature transport data by R. J. Munn, J. Chem. Phys. 42, 3032 (1965); E. A. Mason, R. J. Munn, and F. J. Smith, Discussions Faraday Soc. 40, 27 (1965).

[e]From beam measurements by E. W. Rothe and R. H. Neynaber, J. Chem. Phys. 43, 4177 (1965).

[f]R. J. Bell, Proc. Phys. Soc. (London) 86, 17 (1965); K. L. Bell and A. E. Kingston, Proc. Phys. Soc. (London) 90, 901 (1967).

introduced. However, the most direct procedure would be to employ Eq. (3) and higher α_k coefficients, for the determination of which more extensive refractive-index measurements would be very desirable.

The question of the legitimate continuation of an approximate $\alpha(i\omega)$, as well as other aspects of the theoretical and semiempirical applications of Padé approximants to dynamic polarizabilities and dispersion forces, will be discussed in a subsequent publication.

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[1]For a review, see H. Pauly and J. P. Toennies, Advan. At. Mol. Phys. 1, 195 (1965); see, also, M. L. Klein and R. J. Munn, J. Chem. Phys. 47, 1035 (1967), and references cited therein.

[2]For a review, see A. Dalgarno and W. D. Davison, Advan. At. Mol. Phys. 2, 1 (1966).

[3]G. A. Baker, Jr., in Advances in Theoretical Physics, edited by K. A. Brueckner (Academic Press, Inc., New York, 1965), Vol. I, p. 1.

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[5]H. S. Wall, Analytic Theory of Continued Fractions (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1948), Chaps. XVII and XX.

[6]M. Karplus and H. J. Kolker, J. Chem. Phys. 39, 1493 (1963).

[7]J. A. Baker and P. J. Leonard, Phys. Letters 13, 127 (1964); see, also, A. Dalgarno and A. E. Kingston, Proc. Roy. Soc. (London), Ser. A 259, 424 (1960); A. Dalgarno, I. H. Morrison, and R. M. Pengelly, Intern. J. Quant. Chem. 1, 161 (1967).

[8]R. G. Gordon, private communication.

INSTABILITIES IN A TRAVELING PERIODIC BUMPY THETA PINCH

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A $\beta=1$ theta pinch which, according to Haas and Wesson, would be stabilized by a traveling wave is shown to be unstable. The plasma is described by the incompressible fluid model. It is shown that most of the modes, $m \gtrsim 1.75\delta^{-1}$, are unstable where δ is the ratio of the amplitude of the radius modulation to the mean radius of the pinch.

Recently Haas and Wesson[1] have proposed a new scheme for obtaining a $\beta=1$ toroidal θ pinch which is in equilibrium and stable. Meyer and Schmidt[2] have shown that the outward drift of the plasma due to the curvature of the torus can be suppressed by corrugating the plasma surface. The effect of the alternating regions of good and bad curvature on the stability of the confinement has been studied by Haas and Wesson[3] and Morse[4] using a linear analog to the toroidal configuration. They find that there are instabilities. The new idea of Haas and Wesson is to make the corrugated periodic field travel along the pinch at a velocity V_w. Again using a linear analog configuration, they claim there will now be stability for all modes $m \geq 1$ provided that $V_w > V_a$, where V_a is given by $V_a^2 = B_0^2/\rho$, B_0 being the mean value of the magnetic field at the plasma surface and ρ the plasma density. This result is certainly very surprising. Up to now, in all the proposed schemes of confinement with variable periodic fields[5-8] it has not been possible to obtain stability for any frequency of the field for an ideal fluid. The object of this Letter is to re-examine the equation obtained by Haas and Wesson and show that there are also instabilities in this scheme in the region $m \gtrsim 1.75\delta_0^{-1}$, where δ_0 is the ratio of the amplitude of the wave δR to the mean radius of the pinch R_0.

Let us restate quickly the problem and the notation. The plasma column of radius $R = R_0[1 + \delta(z - V_w t)]$ is confined by the magnetic field $B = B_0 + b(z - V_w t)$, $\delta(z)$ and $b(z)$ being periodic of period L. It is assumed that $L \gg R_0$ and $|\delta| \ll 1$. In the frame of reference of the wave, the field and plasma radius are now functions of z only and the plasma appears to flow with a velocity $V(z)$. Assuming that the plasma can be described by the incompressible-fluid model (Haas and Wesson's hypothesis), V and B are determined by the two equations

$$B^2 + V^2 = \text{const},$$

$$R^2 V = \text{const},$$

where the density has been taken as unity. The equation describing the motion of a surface