Comparison of Measured and Calculated Stark Parameters for Singly Ionized Atoms

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Measured and calculated Stark-broadening parameters are compared for spectral lines emitted by singly ionized atoms from lithium through calcium. It is found that the average value of the ratio of the measured to calculated width is 1.06 $\pm$ 0.05, and the average value of the ratio of the difference between the measured and calculated shift to the measured width is +0.03 $\pm$ 0.07, where the average is over all compared lines. It is shown that only a small error is introduced by using the one-electron approximation (for equivalent electrons) or *LS* coupling. The greatest error arises from the incompleteness (and incorrectness) of tabulated energy levels and their classification.

INTRODUCTION

A comparison has been made between measured[1-31] and calculated Stark-broadening parameters for the spectral lines emitted by singly ionized atoms from lithium through calcium using our semiclassical calculations[32] of the electron-impact broadening of these same ion lines. These calculations are based upon a suitable generalization of the semiclassical methods first introduced for neutral-helium lines.[33] Also, ionized helium lines, as they are subject to the linear Stark effect, must be treated separately; i.e., we only consider "isolated" lines. We have included in our comparison only those lines which satisfy the following criteria: (i) tabulated by Wiese *et al.*[34] in their compilation of oscillator strengths; (ii) no equivalent electrons in the upper (initial) state of the line; (iii) lines for which there exists a sufficient tabulation of the energy levels.[35,36] The first requirement is twofold: first, these are lines for which oscillator strengths are known or at least estimated; second, this seems to give a reasonable (and finite) set of lines with which to work. The second requirement is simply due to the fact that allowing for equivalent electrons is a much harder theoretical problem and is subject to much greater error in analysis. The theory is not yet sufficiently advanced for these calculations to be worthwhile. The third requirement arises from the desirability of reducing the known uncertainty to a reasonable level. Our criterion is that an incompleteness parameter ($\Delta S/S$ as defined below) must be less than, say, 0.5. (This would yield a maximum error of about $\pm 20\%$ in the total width and shift of the corresponding line.)

Our conventions are that w (width) is one-half the separation between half-intensity points, d (shift) is the distance of the profile maximum from the unperturbed ($N_e \to 0$) line, (i, f) are the initial and final states, respectively, and $\bar{f}$ is the average multiplet oscillator strength.

THEORY

The theoretical values for the shift, width, and effective Gaunt factors for these lines come from a semiclassical calculation of the expression[37] for these quantities in the regime where electron-impact broadening dominates ($T_e \simeq 1$–4 eV and $N_e \simeq 10^{16}$–10^{18} cm^{-3}). We have not allowed for ion (quasistatic) broadening in our estimates, nor have we modified the measured values to allow for this effect. In the few cases where it is important, the measured values have been corrected by the original authors. Further, we have used only the authors's estimates to allow for van der Waals broadening[10,37] which is perhaps a more important contribution, especially when argon is used as the carrier gas. In no case, however, are the systematic corrections greater than say 10% and they can be allowed for in a straightforward manner.

Semiclassical calculations of line broadening have been discussed rather widely[37-39]; however, in analogy to Refs. 33 and 40, we have made an important modification to this theory. We have included the "strong collision term" (*ad hoc*) in such a manner that the cutoff parameter ($\rho_{\min}$) is self-consistent at each perturbed velocity and we have insisted that the resulting expressions reduce, in the limits of high temperature (straight perturber orbits) and low temperature, high effective charge (strongly curved perturber orbits) to known forms. That is, we require that the appropriate "phase-shift" limits[40,41] must be attainable with our equations.

The expressions for the width and shift are[32]

$$w_c(v) + id_c(v) = w_s(v) + id_s(v) + w_d(v) + id_d(v) + w_q(v), \tag{1}$$

where

$$\omega_d(v) + id_d(v) = (\lambda^2/30v)(\hbar/m)^2 \left[\frac{2}{3}\,\frac{1}{2l_i+1} \sum_{i' \neq f} l_{ii'} \left|\langle i|r/a_0|i'\rangle\right|^2 \left(a(\delta_{ii'}, \xi_{ii'}) - \frac{i(E_i - E_{i'})}{|E_i - E_{i'}|}\, b(\tfrac{4}{3}\,\delta_{ii'}, \xi_{ii'})\right)\right.$$

$$+\frac{2}{3}\frac{1}{2l_f+1}\sum_{f'\neq f} l_{ff'}|\langle f|r/a_0|f'\rangle|^2\left(a(\delta_{ff'},\xi_{ff'})+\frac{i(E_f-E_{f'})}{|E_f-E_{f'}|}\,b(\tfrac{4}{3}\delta_{ff'},\xi_{ff'})\right)$$

$$+\frac{2\mathcal{R}y\bar{f}}{|E_i-E_f|}\left(1+\frac{2l_f+1}{2l_i+1}\right)\left(a(\delta_{if},\xi_{if})-ib(\tfrac{4}{3}\delta_{if},\xi_{if})\right)\Big], \quad (2)$$

$$w_s(v)+id_s(v)=(\lambda^2/30v)(\hbar/m)^2\tfrac{1}{2}L^2[1.01+(s/|s|)0.74i],$$

$$w_q(v)=(\lambda^2/30v)(\hbar/m)^2\tfrac{1}{15}[(1/\eta L)^2+(3\pi^2/8L^4)] \quad (3)$$

$$\times\Big[(2l_i+1)\begin{pmatrix} l_i & 2 & l_i\\ 0 & 0 & 0\end{pmatrix}^2|\langle i|r^2/a_0^2|i\rangle|^2+(2l_f+1)\begin{pmatrix} l_f & 2 & l_f\\ 0 & 0 & 0\end{pmatrix}^2|\langle f|r^2/a_0^2|f\rangle|^2$$

$$+2(2l_i+1)(2l_f+1)\begin{pmatrix} l_i & 2 & l_i\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_f & 2 & l_f\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix} l_i & 2 & l_i\\ l_f & 1 & l_f\end{Bmatrix}\langle i|r^2/a_0^2|i\rangle\langle f|r^2/a_0^2|f\rangle\Big], \quad (4)$$

where v is the perturbed (electron) velocity, $\mathcal{R}$ is the Rydberg constant, λ is the nominal radiation wavelength, m is the electron mass, L is the perturber angular momentum, and $(s/|s|)$, the sign, is chosen to be the same as that of d_d in Eq. (2). The perturber angular momentum is defined in the usual way: $L=mv\rho_{\min}/h$, where $\rho_{\min}$ is the minimum impact parameter allowed by the unitarity condition and $l_{ii'}=\max(l_i,l_{i'})$. The quantities are all related since $\rho_{\min}\propto A(\xi,\epsilon)$, the free-free scattering function,[42] where the arguments of the functions are $\xi=2\pi cze^2|\Delta E|/mv^3$, $\epsilon=[1+(L/\eta)^2]^{1/2}$, and η is the Coulomb parameter, $\eta=e^2/\hbar v$. Then, by iteration, all of the functions and their arguments must be self-consistent. The expressions are given for $N_e=10^{17}$ cm^{-3} and consequently we renormalized all experimental results to this value, assuming a linear density dependence for the Stark width. For all of these conditions to be satisfied (correct limiting values), we made two changes in the expression for $w+id$: First, in the imaginary part of the weak collision term, $b(\frac{4}{3}\delta,\xi)$ is used instead of $b(\delta,\xi)$; second, the constants in the strong collision term are 1.01 and 0.74 rather than 1.00 and $\tan(\frac{1}{5}\pi)$, respectively. These changes are made so that results are identical with those of Roberts and Davis[41] in the adiabatic straight path ($\epsilon\to\infty$) and strongly curved ($\epsilon\to 1$) limits. Thus w/d may be in error by about 2% in the general straight-path case and by 1% in the adiabatic (but strong-curvature) limit. This is well within errors from other sources, as will be seen.

The expressions for the scattering matrix (for w,d in terms of A, B, etc.) can be integrated analytically[41] over impact parameters [in the notation of Ref. 32, $a(\xi,\epsilon)=\int_{\rho_{\min}}^{\infty}A(\xi,\epsilon)\,d\rho$] with the assumption of no shielding, i.e., $\rho_{\max}$ is taken to be infinity. This procedure yields a set of nonlinear algebraic equations which can be iterated in the usual fashion[43] to yield a self-consistent set of values for w, d, L, and $\rho_{\min}$ for each velocity. The resulting values are then averaged over a Maxwell velocity distribution for the temperatures of interest (Tables I and II and Ref. 32).

An important parameter is $\Delta S/S$ [32] which gives an indication of how complete (in regard to the dipole matrix elements) a particular set of energy levels is. The expression is

$$(\Delta S/S)_{i,f}=\Big\{\sum_{i'}|\langle i|\vec{r}/a_0|i'\rangle|^2+\sum_{f'}|\langle f|\vec{r}/a_0|f'\rangle|^2-R^2\Big\}R^{-2}, \quad (5)$$

and R^2 follows from the usual sum rule for a complete set of states, namely,

$$R^2=(n_i^2/2z^2)[5n_i^2+1-3l_i(l_i+1)]+(n_f^2/2z^2)[5n_f^2+1-3l_f(l_f+1)]. \quad (6)$$

Equation (5) must be summed over all states i' and f' which can contribute to the dipole matrix elements. This is probably the single greatest source of error, namely, that the tabulation of energy levels is not complete. We will use the example of sulfur (multiplet 6, 7) to show what improvement may be obtained by completing the energy-level set (letting $\Delta S/S\to 0$) even if this requires extrapolating the higher levels from a semihydrogenic theory.

An over-all comparison between measured and calculated values can be made by considering the effective Gaunt factors, defined by[44]

$$\bar{g}=w[(\lambda^2/30)(2\pi m/3kT)^{1/2}(\hbar/m)^2\tfrac{2}{3}R^2]^{-1}, \quad (7)$$

TABLE I. Comparison of measured and calculated linewidths. The values for the widths are normalized to an electron density $N_e = 10^{17}$ cm^{-3}. The element, multiplet number, and wavelength (in angström units) are given for each transition. w_c is the calculated value for the width and w_m the corresponding measured value.

Spectrum			T (eV)	w_m (Å)	w_c (Å)	w_m/w_c	$\Delta S/S$	$\bar{g}_m$	Ref.
Be	1	3131	1.4	0.15	0.046	3.26[a]	−0.1	1.34	1
			1.6	0.034	0.042	0.81	−0.1	0.35	2
C	1 uv	1335	1.5	2.7×10^{-3}	1.7×10^{-3}	1.59		0.20	3
	15 uv	2747	1.1	0.91	0.53	1.72	−0.05	0.77	4
	4	3920	1.1	0.41	0.53	0.77	−0.01	0.26	4
			2.2	0.51	0.47	1.09		0.48	5
	6	4267	1.1	1.10	0.95	1.16	−0.01	0.52	4
	7	3361	2.2	0.73	0.93	0.78	−0.02	0.34	5
	8	2993	1.1	2.01	2.17	0.93	−0.03	0.75	4
			2.2	2.58	1.85	1.39		1.31	5
N	1 uv	1085	1.5	1.8×10^{-3}	1.0×10^{-3}	1.80		0.20	3
	5	4623	1.4	0.14	0.18	0.80	−0.44	0.20	28
			1.7	0.14	0.18	0.80		0.20	6
			1.9	0.20	0.17	1.18		0.31	7
			2.0	0.17	0.17	1.00		0.28	8
	18	3007	1.7	0.28	0.22	1.27	+0.08	0.36	6
			2.0	0.30	0.21	1.43		0.56	8
	29	5479	1.7	0.20	0.24	0.82	−0.41	0.18	6
			2.0	0.29	0.25	1.16		0.26	8
	30	3843	1.7	0.58	0.39	1.44	+0.23	0.52	6
			1.9	0.44	0.38	1.16		0.42	7
			2.0	0.50	0.37	1.35		0.54	8
Mg	1 uv	2795	1.0	0.06	0.05	1.29	0.00	0.37	9
			1.6	0.044	0.044	1.00		0.32	10
			1.6	0.025	0.045	0.52		0.17	11
			2.4	0.037	0.040	0.93		0.35	12
			3.0	0.035	0.039	0.94		0.35	12
	4	4481	1.0	1.05	1.30	0.81	−0.01	0.42	10
Si	1	3858	0.8	0.20	0.60	0.33[a]	0.02	0.18	12
	2	6355	0.7	0.66	1.26	0.52	0.01	0.19	12
	4	5972	0.9	1.20	1.29	0.93	−0.09	0.22	13
	6	3338	0.9	1.50	1.00	1.50	−0.05	0.24	13
S	6	5468	1.0	0.26	0.31	0.84	−0.32	0.20	13
			1.0	0.30	0.31	0.97		0.20	14
	7	4361	1.0	0.34	0.24	1.42	−0.51	0.19	13
			1.0	0.38	0.24	1.58		0.19	14
Cl	1	4806	1.6	0.20	0.22	0.91	−0.03	0.19	15
	2	5438	1.6	0.24	0.22	1.09	−0.28	0.20	15
	3	5221	1.6	0.23	0.28	0.82	−0.48	0.21	15
A	1	4388	2.7	0.14	0.12	1.17	−0.21	0.42	16
	2	3968	2.7	0.16	0.10	1.60	−0.33	0.51	16
	6	4875	1.0	0.15	0.21	0.71	−0.32	0.15	16
			1.0	0.18	0.21	0.86		0.19	29
			1.1	0.18	0.21	0.86		0.19	17
			1.2	0.14	0.20	0.70		0.16	18
			1.6	0.18	0.18	1.00		0.25	19
			2.6	0.20	0.16	1.26		0.19	20
			2.6	0.20	0.16	1.26		0.38	21
	7	4361	1.1	0.16	0.17	0.94	−0.35	0.20	29
			1.1	0.17	0.17	1.00		0.20	17
			1.2	0.13	0.17	0.77		0.11	18
			1.6	0.18	0.16	1.13		0.27	19
			2.6	0.18	0.14	1.29		0.38	20
			2.6	0.14	0.14	1.00		0.29	21

TABLE I. (*Continued*)

			T (eV)	w_m (Å)	w_c (Å)	w_m/w_c	$\Delta S/S$	$\bar{g}_m$	Ref.
	10	3801	1.1	0.13	0.13	1.00	−0.52	0.20	17
			1.1	0.13	0.13	1.00		0.20	29
			1.6	0.55	0.11	5.00[a]		1.10	19
			2.6	0.16	0.10	1.60		0.42	19
	14	4898	1.1	0.21	0.23	0.91	−0.37	0.20	29
			1.2	0.19	0.23	0.83		0.19	18
			2.6	0.24	0.20	1.20		0.17	20
			2.6	0.25	0.20	1.25		0.39	21
Ca	1	3945	1.0	0.10	0.14	0.71	−0.05	0.18	9
			1.0	0.61	0.14	4.37[a]		1.09	23
			1.0	0.06	0.14	0.43[a]		0.11	24
			1.1	0.07	0.14	0.50		0.13	25
			1.5	0.51	0.12	4.25[a]		1.28	26
			1.4	0.09	0.12	0.83		0.25	11
			1.6	0.09	0.12	0.75		0.23	27
			1.7	0.09	0.12	0.75		0.23	10
			2.2	0.05	0.11	0.45[a]		0.15	25
			2.3	0.10	0.11	0.92		0.31	11
	2	8579	1.0	0.17	0.68	0.25[a]	−0.19	0.08	9
	3	3727	1.0	0.45	0.35	1.29	−0.05	0.34	23
			1.5	0.55	0.32	1.72		0.50	26
	4	3173	1.0	0.37	0.26	1.42	−0.03	1.38	23

[a]Values not used in the average since there was a greater than factor of 2 discrepancy between w_c and w_m.

where T is the temperature. The resulting values can be plotted versus $kT/\Delta E$, the thermal energy divided by the energy separation between the *upper* electron (i) level and the nearest perturbing level (i') (in the sense of energy); i.e., $kT/\Delta E = \max\{i'\} \times (kT/|E_i - E_{i'}|)$, where E_i is the energy of a particular level, and can be compared with accepted values.[32]

RESULTS

The results of these calculations are tabulated completely in Ref. 32. The experimental data and corresponding theoretical calculations are presented in Tables I and II. In addition, we have listed the measured effective Gaunt factors [Eq. (7)] for these lines and these are also given in Table I. If the theory of electron-impact broadening is not sufficient to account for the line shapes (that is, if there is a systematic error) then we expect w_m/w_c and $(d_m - d_c)/\omega_m$ to differ from 1.0 and 0.0, respectively. The actual values are

$$\langle w_m/w_c \rangle = 1.06 \pm 0.05$$

and

$$\langle (d_m - d_c)/w_m \rangle = +0.03 \pm 0.07,$$

where the angular bracket notation indicates an average over all available data. This comparison is analogous to a previous result[45] but much more accurate and certainly more complete.

ERRORS

The following are possible sources of error: (i) lack of symmetrization[46] of the scattering function $a(\xi, \epsilon)$; (ii) no allowance for equivalent electrons; (iii) incomplete set of energy levels; (iv) use of LS coupling only; (v) no allowance for shielding effects.

Of these, the only error which contributes significantly is that due to the incomplete set of energy levels (which has a secondary connection with the type of coupling). Symmetrization may contribute somewhat to a decrease in the apparent widths, but it is not clear that this is a "real" effect,[46,47] especially in light of the fact that in most cases the elastic contribution to the width and shift is at least 50%.[32] No allowance is made for equivalent electrons since we have done calculations only for those lines for which the upper level (certainly the more important of the initial and final levels) has no equivalent electrons. We allowed the lower level to have equivalent electrons, but because the primary contribution involving the lower level arises from its interaction with the upper level, and since we use tabulated oscillator strengths ($\bar{f}$) (for the dipole matrix elements) to reduce the error which arises from calculation of these matrix elements, the error associated with equivalent electrons should be very small. Shielding effects are negligible since $\lambda_{\text{Debye}} \simeq 300$ Å and the strong-collision parameter $\rho_{\min} \lesssim 10$ Å in most cases. In

addition, most of the contribution to the weak-collision term ($\gtrsim 95\%$) comes from within a ~ 100-Å sphere which can be seen from examination of the $a(\xi,\epsilon)$ and $b(\xi,\epsilon)$ scattering functions. The final source of error for these comparisons enters through the use of LS coupling. This is not an independent error. It is tied up with the completeness of the energy levels. If the energy-level set were complete, then sum rules would tell us that the type of coupling is unimportant since the results would be almost identical, at least for the widths, independent of the coupling scheme used. However, when the energy-level set is not complete, JK coupling could be important for some of the atoms (especially for the higher-lying levels of argon). In all cases, with the exception of the higher-lying levels of argon, however, either LS coupling is a good approximation, or the set of energy levels is sufficiently complete for this source of error to be negligible.

Thus we are left with the primary source of error: the incompleteness of the set of energy levels. We can check on this effect by using two adjacent lines, namely, those of sulfur, multiplet 6 and 7, which have similar structure, but different perturbing levels. The agreement between measurement and theory for these lines is quite different for the two, concomitant with differing $\Delta S/S$'s. The energy levels extend far enough from the ground state that we can use a semihydrogenic

TABLE II. Comparison of measured and calculated line shifts. The values of the shifts are normalized to an electron density $N_e = 10^{17}$ cm^{-3}. The element, multiplet number, and wavelength (in angström units) are given for each transition.

Spectrum			T (eV)	d_m (Å)	d_c (Å)	$\lvert d_m\rvert/w_m$	$(d_m-d_c)/w_m$	Ref.
Be	1	3131	1.4	−0.03	−0.04	0.88[a]	−0.24[a]	30
N	5	4623	1.7	0.16	0.14	1.14	−0.14	6
	18	3007	1.7	0.36	0.21	1.71	+0.50	6
	29	5479	1.7	0.15	0.21	0.73	−0.30	6
	30	3843	1.7	0.55	0.30	0.95	+0.43	6
			1.9	0.80	0.27	1.82	+1.20[b]	7
Mg	1 uv	2795	1.4	0.012	−0.031	0.60[c]	+0.86[a]	11
			1.8	0.016	−0.028	0.70[c]	+1.10[a,b]	11
	2 uv	2934	1.4	0.08	0.15	0.57[c]	−0.45	30
A	1	4388	1.2	0.06[d]	0.10	0.26	−0.28	31
	2	3968	1.2	0.09[d]	0.08	0.44	+0.06	31
	6	4875	1.0	−0.07	−0.09	0.40	+0.11	16
			1.2	−0.08	−0.07	0.46	−0.06	18
			1.2	−0.09[d]	−0.07	0.51	−0.11	31
			2.3	−0.04	−0.01	0.22[c]	−0.23	22
			2.6	−0.08	−0.01	0.46	−0.40	20
			2.8	−0.02	+0.00	0.12[c]	−0.11	22
			3.3	−0.01	+0.01	0.06[c]	−0.11	22
			3.7	−0.01	+0.01	0.01[c]	−0.11	22
	7	4361	1.2	−0.05[d]	−0.08	0.19	+0.15	31
			1.2	−0.03	−0.08	0.19	+0.30	18
			2.6	−0.05	−0.00	0.31	−0.31	20
	10	3801	1.2	−0.00[d]	+0.09	0.00	−0.70	31
	14	4898	1.2	−0.05[d]	−0.17	0.26	+0.63	31
			1.2	−0.04	−0.17	0.21	+0.68	18
			2.6	−0.08	−0.13	0.31	+0.20	20
Ca	1	3945	1.0	−0.02	−0.12	0.25[a]	+1.00[a,b]	24
			1.2	−0.09	−0.11	1.13	+0.25	30
			1.4	−0.02	−0.11	0.25	+1.13[b]	11
			2.2	−0.03	−0.09	0.60	+0.80	11
	3	3727	1.2	0.18	0.35	0.38	−0.36	30
			1.5	0.25	0.32	0.45	−0.13	26
	4	3173	1.2	0.18	0.25	0.49	−0.20	30

[a]A calculated or averaged value for the width of a line is used in cases for which no width measurement is available or where the width measurements are believed to be in error (differ by a factor of 5 from other values).

[b]These values are not included in the average for the cases where $\Delta d/w_m$ is greater than a factor of 2.

[c]These shift to width ratios are taken directly from the references.

[d]We allow for a change owing to the necessity of doing an Abel inversion.

theory (to obtain the subsequent spacings for a given series) to reduce $\Delta S/S$ to zero. By using $N = 2 \rightarrow 8$, where N is the number of levels used in the calculation, we can plot w vs $\Delta S/S$ and we find (see results in Table III) that there is a limiting (asymptotic) value for w which agrees quite well with the measurements.

TABLE III. Comparison of calculated width vs energy level completeness. A comparison of w_c for various values of $\Delta S/S$. The units of w_m and w_c are angströms.

			$N=2$			$N=8$		
Spectral line	$\langle w_m \rangle$	w_c	$\Delta S/S$	w_c/w_m	w_c	$\Delta S/S$	w_c/w_m	Ref.
$S(6)$	0.28	0.31	−0.64	0.90	0.31	−0.01	0.90	13,14
$S(7)$	0.36	0.24	−0.75	1.50	0.27	−0.04	1.24	13,14

CONCLUSION

From the results shown in Tables I and II it would appear that in this temperature and density regime, the semiclassical calculation of the expressions for the width, shift, and average Gaunt factor of isolated spectral lines from singly ionized atoms caused by electron impacts are quite adequate. Thus, at least for the widths, the situation is about as good as for the neutral lines.[33,36,37,48] The errors seem to be random, and caused by uncertainties in both the calculations and measurements. If there were systematic problems with the theory, such as polarization of the ions by the plasma, then we would expect $\langle w_m/w_c \rangle$ and $\langle (d_m - d_c)/\omega_m \rangle$ to differ from 1.0 and 0.0, respectively.

Part of the uncertainty which we do find (which is completely random in nature with both the second and third error moments[49] being small) is due to the fact that many of these lines are very narrow and thus are quite difficult to measure. This can be seen explicitly in the argon measurements where the variation from experiment to experiment (for a given line) is considerably larger than the average variation. Most of this uncertainty, however, is due simply to the difficulty of the actual measurement of line profiles as narrow as these, and not to gross experimental uncertainties. Other problems, such as allowance for other broadening mechanisms, are not serious and can be made in a straightforward manner. In the few cases (see Tables I and II) where we felt there was an important error in the measurements, there was usually disagreement with the other experimental measurements and with calculated values by more than a factor of 2. Thus this is the criterion we used to eliminate a few (12 out of 113) of the width and shift measurements.

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Retarded van der Waals Forces at All Distances Derived from Classical Electrodynamics with Classical Electromagnetic Zero-Point Radiation

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The van der Waals forces between a polarizable particle and a conducting wall and between two polarizable particles are calculated within the theory of classical electrodynamics with classical electromagnetic zero-point radiation. This theory assumes the differential equations of traditional classical electrodynamics but changes the homogeneous boundary condition on Maxwell's equations to correspond to the presence of random classical electromagnetic radiation with a Lorentz-invariant spectrum. The van der Waals force calculations are performed exactly within the nonrelativistic equations of motion for the particles represented as point-dipole oscillators. The classical results are found to agree identically to all orders in the fine-structure constant α with the nonrelativistic quantum electrodynamic calculations of Renne. To fourth order, there is agreement with the perturbation-theory work of Casimir and Polder.

I. INTRODUCTION

In work published recently,[1,2] it has been shown that the short- and long-range asymptotic limits for interatomic van der Waals forces can be calculated from a simple classical model. Picturing atoms or molecules in the Drude–Lorentz approximation as classical dipole oscillators, one can understand the van der Waals forces between a neutral polarizable particle and a conducting wall or between two neutral polarizable particles as due to classical electromagnetic interactions when the particles are immersed in random classical radiation with a Lorentz invariant spectrum. In two previous articles, the unretarded London force[2] when the particle separation $R \to 0$, and the asymptotic retarded force[1] when $R \to \infty$ were evaluated and found to agree exactly with quantum calculations; the present work extends the agreement between the theories for these forces to the entire range of separations R. The full fourth-order Casimir–Polder formula[3] from quantum electrodynamics has thus been obtained from a purely classical theory of electromagnetism.

There has been continuing interest in van der Waals forces within both physics and chemistry, and recently even attention to applications of van der Waals forces in biological systems. However, the present article does not produce any new formula for application to a specific situation. Rather the calculation here represents a further step in a general program in theoretical physics. The program is intended to discover just how much of the physics which is presently regarded as dependent upon the notion of discrete quanta can actually be understood within a specific theory of purely classical electromagnetism. The theory, which we have termed classical electrodynamics with classical electromagnetic zero-point radiation, adopts the differential equations of traditional classical electrodynamics but changes the homogeneous boundary condition on Maxwell's equations to correspond to the presence of random classical electromagnetic radiation with a Lorentz invariant spectrum. Thus far, a number of phenomena within statistical thermodynamics have been analyzed in terms of this theory—including the blackbody-radiation spectrum,[4] the fluctuations usually ascribed to photon statistics,[5] the third law of thermodynamics,[6] and oscillator and rotator specific heats.[7] Marshall has applied the theory to the van der Waals forces between macroscopic objects.[8]