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Quantum Corrections to the Second Dielectric Virial Coefficient of Rare-Gas Atoms* †

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An expression is derived for the first quantum correction to the second dielectric virial coefficient of interacting rare-gas atoms. It is shown that this correction is not large enough to account for the experimently determined negative values of this quantity for helium and neon. Based on this result, along with a previously established argument, it is concluded that the point-dipole approximation is the likely cause of the discrepancy between the theoretical and experimental results.

I. INTRODUCTION

It is well known that at high pressures nonpolar gases show slight deviations from the Clausius–Mossotti relation

$$(\epsilon-1)/(\epsilon+2)=(4\pi\bar{\alpha}/3)\rho,$$

where $\bar{\alpha}$ is the mean atomic polarizability. These deviations are due to intermolecular interactions and have been discussed in considerable detail.[1–5] The normal theoretical treatment for dense gases is to expand the Clausius–Mossotti relation in terms of the number density ρ, viz.,

$$(\epsilon-1)/(\epsilon+2)=(4\pi\bar{\alpha}/3)\rho+B_D\rho^2+C_D\rho^3+\cdots,$$

where $B_D, C_D, \cdots$ are the second, third, $\cdots$, etc., dielectric virial coefficients. For spherical molecules it can be shown in general that

$$B_D=\frac{8\pi^2}{3}\int_0^\infty drr^2\alpha(r)\exp\left(-\frac{\phi(r)}{kT}\right), \qquad (1)$$

where $\phi(r)$ is the intermolecular potential and $\alpha(r)$ is the spherical average polarizability increment

$$\alpha(r)=\tfrac{1}{3}[\alpha_{||}(r)+2\alpha_{\perp}(r)]-2\bar{\alpha}, \qquad (2)$$

with $\alpha_{\perp}(r)$ and $\alpha_{||}(r)$ being the transverse and longitudinal components of the polarizability at an internuclear separation r. In the commonly used point-dipole approximation, $\alpha(r)$ becomes $4\bar{\alpha}^3r^{-6}$, which always yields a positive second dielectric virial coefficient. Prompted by the negative experimental value of B_D obtained by Orcutt and Cole[6] for helium and neon, Levine and McQuarrie[7] suggested that the use of the point-dipole approximation in Eq. (1) wasn't adequate and that the more general form (2) must be used for the polarizability in Eq. (1). Later, DuPré and McTague,[8] using the $^3\Sigma$ state of H_2 as a model for colliding pairs of rare-gas atoms, demonstrated that $\alpha(r)$ can indeed become negative at intermediate internuclear separations, thereby making it theoretically plausible for B_D to be a negative quantity.

One remaining question is that of the possible existence of anomalously high quantum corrections to the dielectric virial coefficients for He and Ne. In this paper, the first quantum correction is evaluated using the formalism of Kirkwood[9] and techniques presented earlier by Isihara and Hanks.[10] Rather than using the exact form for $\alpha(r)$, we use the point-dipole approximation. The reason for doing this is that we are looking for abnormally large corrections and at worst, the point-dipole approximation should only be off by a factor of 2 or 3. This error weighed against the resulting simplification of the problem makes it an appropriate choice.

II. FORMULATION

If we consider an imperfect gas in a parallel plate capacitor, we can express the ordinary (pressure) virial coefficients[11] as functions of the electric displacement D as

$$B_n(T,D)=B_n^{(0)}(T)+B_n^{(2)}(T)D^2+B_n^{(4)}(T)D^4+\cdots,$$

where we have realized that the coefficients must be even functions of D. To obtain the second dielectric virial coefficient B_D, we make use of imperfect gas theory to obtain $B_2^{(2)}(T)$ and then use the relation[3]

$$B_D(T)=-(8\pi kT/3)B_2^{(2)}(T)+(32\pi^2\bar{\alpha}^2/9), \qquad (3)$$

where k is the Boltzmann constant and T is the temperature.

Following the development of Kirkwood,[9] we may write the canonical partition function as

$$Q_N(V,T,D)=(N!h^{3N})^{-1}\int\cdots\int\exp(-\beta H_N)\times\left[\sum_{l=0}^{\infty}w_l(\mathbf{r},\mathbf{p},\beta)\hbar^l\right]d\mathbf{r}d\mathbf{p},$$

where $\hbar$ is Planck's constant divided by 2π, $\beta=1/kT$, $\mathbf{r}$ and $\mathbf{p}$ stand for the set of all N spatial coordinates and conjugate momenta, and

$$d\mathbf{r}d\mathbf{p}=\prod_{i=1}^{N}d\mathbf{r}_id\mathbf{p}_i.$$

It can be easily shown that the contributions to Q_N resulting from the terms in the sum which are odd in l vanish, and it is also easily seen that $w_0=1$. Keeping only terms through $\hbar^2$, we have

$$Q_N(V,T,D)=(N!h^{3N})^{-1}\int\cdots\int\exp(-\beta H_N)\times[1+w_2\hbar^2+O(\hbar^4)]d\mathbf{r}d\mathbf{p}. \qquad (4)$$

In these equations H_N is the complete classical Hamiltonian for the system of rare-gas atoms, which, using the notation of McQuarrie and Levine,[4] can be written as

$$H_N=\sum_{k=1}^{N}\frac{p_k^2}{2m}+\phi_N(r)-\tfrac{1}{2}\mathbf{D}\cdot\boldsymbol{\alpha}\cdot(1-\boldsymbol{\alpha}\cdot\mathbf{T})^{-1}\cdot\mathbf{D}$$
$$=K(p)+U(r),$$

where $\phi_N(r)$ is the potential energy without the external field, $\boldsymbol{\alpha}$ is a supermatrix whose elements are the polarizability tensors of the molecules 1 through N, and $\mathbf{T}$ is a supermatrix whose elements are the dipole–dipole interaction tensors given by

$$T_{\alpha\beta}(r_{ij})=(3r_{ij\alpha}r_{ij\beta}-r_{ij}^2\delta_{\alpha\beta})/r_{ij}^5,$$

with $\mathbf{r}_{ij}$ being the vector distance between the ith and jth particles.

The first quantum correction to $Q_N(V,T,D)$, i.e., w_2, is given by

$$w_2=-\frac{\beta^2}{2m}\left\{\tfrac{1}{2}\sum_{k=1}^{N}\nabla_k^2U-\tfrac{1}{3}\beta\Big[\sum_{k=1}^{N}(\nabla_kU)^2+m^{-1}\Big(\sum_{k=1}^{N}\mathbf{p}_k\cdot\nabla_k\Big)^2U\Big]+\frac{\beta^2}{4m}\Big(\sum_{k=1}^{N}\mathbf{p}_k\cdot\nabla_kU\Big)^2\right\}.$$

If we restrict ourselves to consider terms of order D^2 or less, we can write

$$w_2=w_2^{(0)}+w_2^{(2)}D^2+O(D^4)$$

and

$$Q_N(V,T,D)=Q_N^{(0)}(V,T)+Q_N^{(2)}(V,T)D^2+O(D^4). \tag{5}$$

Since we are only interested in the second virial coefficients, we only need to evaluate Q_1 and Q_2. It can easily be shown that[4]

$$Q_1(V,T,D)=(V/\Lambda^{3/2})[1+\tfrac{1}{2}(\beta\bar{\alpha})D^2+O(D^4)], \tag{6}$$

where Λ is the de Broglie thermal wavelength. To evaluate Q_2, we express the Hamiltonian for two particles as

$$H_2=H_2^{(0)}+u(r)D^2,$$

where we have chosen the z direction to be parallel with the electric displacement so that

$$u(r)=-[\bar{\alpha}+\bar{\alpha}^2T_{zz}+\bar{\alpha}^3T_{z\gamma}T_{z\gamma}+O(\bar{\alpha}^4)],$$

and it is to be understood that all greek subscripts are to be summed. We now expand the part of the Boltzmann factor in Eq. (4) depending on D. This procedure yields

$$Q_2^{(0)}(V,T)=(1/2h^6)\iiiint\exp(-\beta H_2^{(0)})\times[1+\hbar^2w_2^{(0)}+O(\hbar^4)]d\mathbf{r}d\mathbf{p}$$

and

$$Q_2^{(2)}(V,T)=-(1/2h^6)\iiiint\exp(-\beta H_2^{(0)})\times[\beta u(r)+\beta\hbar^2u(r)w_2^{(0)}-\hbar^2w_2^{(2)}]d\mathbf{r}d\mathbf{p}. \tag{7}$$

Using Eqs. (5) and (6) with $D=0$, we are directly led to the well-known result[12]

$$B_2(T,D=0)=-2\pi\int_0^\infty drr^2f(r)+\frac{h^2}{24\pi mk^3T^3}\times\int_0^\infty dr[r\phi'(r)]^2\exp[-\beta\phi(r)],$$

where N_0 is Avogadro's number and $f(r)$ is the Mayer f function. The prime indicates differentiation with respect to the argument. The D^2 term gives

$$B_2^{(2)}(T)=(\beta\bar{\alpha}\Lambda^3/V)Q_2^{(0)}(V,T)-(\Lambda^3/V)Q_2^{(2)}(V,T). \tag{8}$$

Upon substituting into Eq. (7) for u, $w_2^{(0)}$, and $w_2^{(2)}$ and then using Eq. (8), we find that

$$B_2^{(2)}(T)=B_2^{(2)cl}(T)-\frac{h^2\bar{\alpha}}{24\pi mk^4T^4}\times\int_0^\infty dr[r\phi'(r)]^2\exp[-\beta\phi(r)]-I(T)-J(T),$$

where $B_2^{(2)cl}(T)$, $I(T)$, and $J(T)$ are given by

$$B_2^{(2)cl}(T)=\frac{4\pi\bar{\alpha}^2}{3kT}-\frac{4\pi\bar{\alpha}^2}{kT}\int_0^\infty drr^{-4}\exp[-\beta\phi(r)],$$

$$I(T)=-\frac{h^2}{48\pi^2mk^2T^2}\int d\mathbf{r}[\nabla^2u-\beta(\nabla\phi\cdot\nabla u)]\times\exp[-\beta\phi(r)]$$
$$=\frac{5h^2\bar{\alpha}^3}{m\pi k^2T^2}\int_0^\infty drr^{-6}\exp[-\beta\phi(r)]+\frac{h^2\bar{\alpha}^3}{m\pi k^3T^3}\times\int_0^\infty drr^{-5}\exp[-\beta\phi(r)]\phi'(r),$$

and

$$J(T)=(h^2/48\pi^2mk^3T^3)\int d\mathbf{r}[\nabla^2\phi-\tfrac{1}{2}\beta(\nabla\phi\cdot\nabla\phi)]u(r)\times\exp[-\beta\phi(r)].$$

The expression $J(T)$ reduces to

$$J(T)=-\frac{\bar{\alpha}h^2}{24\pi mk^4T^4}\int_0^\infty dr[r\phi'(r)]^2\exp[-\beta\phi(r)]-\frac{\bar{\alpha}^3h^2}{12\pi mk^4T^4}\int_0^\infty drr^{-4}\phi'^2(r)\exp[-\beta\phi(r)]-\frac{\bar{\alpha}^3h^2}{\pi mk^3T^3}\int_0^\infty drr^{-5}\phi'(r)\exp[-\beta\phi(r)].$$

Combining these terms we obtain

$$B_2^{(2)}(T)=B_2^{(2)cl}(T)+\frac{\bar{\alpha}^3h^2}{12\pi mk^4T^4}\int_0^\infty drr^{-4}\phi'^2(r)\times\exp[-\beta\phi(r)]-\frac{5\bar{\alpha}^3h^2}{\pi mk^2T^2}\int_0^\infty drr^{-6}\exp[-\beta\phi(r)].$$

Using Eq. (3), we have then, for the second dielectric virial coefficient

$$B_D(T)=B_D^{cl}(T)-\frac{2\bar{\alpha}^3h^2}{9mk^3T^3}\int_0^\infty drr^{-4}\phi'^2(r)$$

$$\times\exp[-\beta\phi(r)]+\frac{40\bar{\alpha}^3h^2}{3mkT}\int_0^\infty drr^{-6}\exp[-\beta\phi(r)].$$

If we use a zero field intermolecular potential of the Lennard-Jones type, we may write this equation in reduced form, viz.,

$$B_D^*(T^*)\equiv B_D(T^*)/b_0^2$$

$$=B_D^{*cl}(T^*)+\Lambda^{*2}B_{D,I}^*(T^*)+O(\Lambda^{*4}),$$

where

$$b_0=2\pi\sigma^3/3,\qquad T^*=kT/\epsilon,\quad\text{and}\quad \Lambda^{*2}=h^2/\sigma^2m\epsilon.$$

The undefined parameters are ϵ and σ which correspond to the well-depth and hard-sphere diameter of the Lennard-Jones potential. Using these definitions with a (6, 12) potential we obtain

$$B_D^{*cl}(T^*)=24\alpha^{*3}\int_0^\infty dxx^{-4}\exp\left(\frac{\phi^*(x)}{T^*}\right)$$

and

$$B_{D,I}^*(T^*)=-\frac{8\alpha^{*3}}{\pi^2T^{*3}}\int_0^\infty dx(12x^{-15}-6x^{-9})^2$$

$$\times\exp\left(-\frac{\phi^*(x)}{T^*}\right)+\frac{30\alpha^{*3}}{\pi^2T^{*2}}\int_0^\infty dxx^{-6}\exp\left(-\frac{\phi^*(x)}{T^*}\right),$$

where

$$x=r/\sigma,\qquad \alpha^*=\bar{\alpha}/\sigma^3,\quad\text{and}\quad \phi^*(x)=4(x^{-12}-x^{-6}).$$

This expression was evaluated numerically along with the expression for the quantum corrected pressure virial coefficient with $D=0$, the results of which are presented in the next section.

III. RESULTS AND DISCUSSION

Table I gives the values of the Lennard-Jones parameters and Λ^* for the various elements considered in this calculation. Table II displays the results of the calculations for both the pressure virial coefficient with no field and the second dielectric virial coefficient at various reduced temperatures. It should be pointed out that Table 6.5-1 in Ref. 12 is somewhat inaccurate. This was confirmed by calculating the quantum correction by both the method presented in that reference and by the numerical integration indicated in this work.

We see that for helium at a reduced temperature of $T^*=30(\sim 33\ \text{C}^\circ)$ that the first quantum correction is approximately 1.43%, and for neon with $T^*=9(\sim 47°\text{C})$ the correction is approximately 0.25%, which are

TABLE I. Values of ϵ/k, σ, N_0b_0, and Λ^* for rare gases.

Element	σ	ϵ/k	N_0b_0	Λ^*
He	2.556	10.22	21.065	2.677
Ne	2.749	35.60	26.206	0.593
A	3.405	119.80	49.799	0.186

TABLE II. Values of $B_2^{*cl}(T^*)$ and $B_D^{*cl}(T^*)$ and their first quantum corrections.

T^*	$B_2^{*cl}(T^*)$	$B_{2,I}^*(T^*)$	$10^3B_D^{*cl}(T^*)$	$10^4B_{D,I}^*(T^*)$
0.75	−4.175842	0.868561	1.367644	−3.205340
0.80	−3.734150	0.729109	1.296858	−2.711038
0.85	−3.363049	0.621888	1.238647	−2.328668
0.90	−3.047065	0.537683	1.190075	−2.026646
0.95	−2.774866	0.470332	1.149040	−1.783780
1.00	−2.538039	0.415599	1.113996	−1.585435
1.05	−2.330193	0.370495	1.083787	−1.421241
1.10	−2.146349	0.332866	1.057531	−1.283688
1.15	−1.982632	0.301127	1.034545	−1.167224
1.20	−1.835939	0.274094	1.014292	−1.067673
1.25	−1.703769	0.250864	0.996343	−0.981846
1.30	−1.584103	0.230743	0.980355	−0.907275
1.35	−1.475260	0.213189	0.966047	−0.842022
1.40	−1.375850	0.197772	0.953190	−0.784552
1.45	−1.284724	0.184150	0.941592	−0.733635
1.50	−1.200899	0.172048	0.931095	−0.688278
1.55	−1.123537	0.161240	0.921564	−0.647670
1.60	−1.051929	0.151543	0.912886	−0.611146
1.65	−0.985473	0.142805	0.904965	−0.578152
1.70	−0.923641	0.134898	0.897716	−0.548230
1.75	−0.865976	0.127717	0.891069	−0.520994
1.80	−0.812064	0.121172	0.884962	−0.496116
1.85	−0.761568	0.115187	0.879342	−0.473320
1.90	−0.714179	0.109698	0.874159	−0.452370
1.95	−0.669627	0.104648	0.869375	−0.433061
2.00	−0.627664	0.099991	0.864951	−0.415218
2.10	−0.550677	0.091692	0.857062	−0.383340
2.20	−0.481754	0.084531	0.850273	−0.355738
2.30	−0.419722	0.078300	0.844414	−0.331643
2.40	−0.363626	0.072837	0.839342	−0.310453
2.50	−0.312662	0.068016	0.834946	−0.291694
2.60	−0.266190	0.063734	0.831130	−0.274985
2.70	−0.223647	0.059910	0.827818	−0.260022
2.80	−0.184562	0.056477	0.824945	−0.246553
2.90	−0.148563	0.053381	0.822456	−0.234373
3.00	−0.115299	0.050577	0.820304	−0.223312
3.10	−0.844757	0.048027	0.818450	−0.213226
3.20	−0.558533	0.045699	0.816861	−0.203998
3.30	−0.292114	0.043568	0.815506	−0.195524
3.40	−0.434966	0.041609	0.814361	−0.187720
3.50	0.188807	0.039804	0.813404	−0.180510
3.60	0.406498	0.038136	0.812616	−0.173833
3.70	0.610703	0.036591	0.811979	−0.167632
3.80	0.802589	0.035156	0.811479	−0.161859
3.90	0.983151	0.033820	0.811102	−0.156473
4.00	0.115344	0.032573	0.810838	−0.151437
4.10	0.131412	0.031408	0.810676	−0.146719
4.20	0.146612	0.030316	0.810606	−0.142290
4.30	0.160987	0.029292	0.810620	−0.138125
4.40	0.174611	0.028330	0.810711	−0.134202

approximately the same magnitude as the quantum corrections to the pressure virial coefficients. Thus we can conclude that anomalously low (even negative) experimental values of the second dielectric virial coefficients of rare gases are due to the use of the point-dipole approximation for $\alpha(r)$.

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$$p=kT\sum_{n\geq 2}B_n(T,D)\rho^n,$$

and should not be confused with the dielectric virial coefficients B_D, C_D, etc., given by the expansion of the Clausius–Mossotti function.
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Zeeman Effect in Porphyrins: Zero-Field Splitting of the Excited Electronic States*

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Recent experimental studies have reported anomalous and contradictory results for the absorption of left and right circularly polarized light (LCPL and RCPL) by zinc and magnesium coproporphyrins in the presence of a magnetic field: for both compounds, the absorption bands for right and left circularly polarized light have distinctly different shapes at room temperature; at 77°K unexplained shoulders appear in the absorption spectra for both polarizations for the magnesium but not for the zinc compound; the value of the angular momentum of the lowest energy excited state computed from the separation of the peaks of the LCPL and RCPL absorption bands differs from the value obtained from magnetic circular dichroism (MCD) experiments by nearly 50%; no shape anomalies were observed in the MCD spectra. We derive a general solution for the mixing of two states by a magnetic field and show that all of the anomalous experimental data are explained if (a) the presumably degenerate pair of excited states are split in zero field by an energy comparable to the Zeeman energy but less than the spectral bandwidths, and also (b) the overlapping transitions have unequal intensities. Our results show that MCD should give better estimates of excited state angular momenta while the direct measurement of LCPL and RCPL is superior in detecting nondegeneracy.

INTRODUCTION

Malley[1] and Malley, Feher, and Mauzerall[2] recently measured the Zeeman effect on the visible absorption bands of zinc and magnesium coproporphyrin. Their data for the absorption of right and left circularly polarized light (RCPL and LCPL) by transitions to the lowest excited states ($Q_{0\leftarrow 0}$ band[3]) of zinc coproporphyrin I are shown in Fig. 1. These data show asymmetries between the LCPL and RCPL absorption curves which are not predicted by simple theory[3,4] and for which Malley *et al.*[1,2] offered no explanation. In the presence of a magnetic field, the RCPL band shifts to lower energy, exhibits a higher peak intensity, and is narrower than is the LCPL band. Significantly, the areas under the two curves are equal. This result was found for both isomers I and III of zinc coproporphyrin (see Fig. 2) in a variety of solvents at room temperature and at 77°K. At room temperature, the spectra of magnesium coproporphyrin I were similar to the data shown in Fig. 1. At 77°K, however, shoulders appeared on both the LCPL and RCPL absorption bands, another result which was not explainable.[1,2]

Malley *et al.*[1,2] calculated the angular momentum, M_z, of the lowest excited state from the separation between the peaks of the LCPL and RCPL absorption curves. At room temperature they found about 9 units of angular momentum for both isomers and both metals. This value is in excellent agreement with the predictions of simple free electron theory[3,4] but greater than the value calculated from molecular orbital theory by about a factor of 2.[5] At 77°K the value of M_z decreased to about 6.4 for the zinc compound but increased for the magnesium compound.