A Relation between the Electric and Diamagnetic Susceptibilities of Monatomic Gases

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A relation is derived by quantum-mechanical perturbation theory, using a center of gravity argument and the Kuhn-Reiche sum rule, between the polarizability and diamagnetic susceptibility of monatomic gases. On comparison with a similar paper by Kirkwood, who uses a variational method, a criterion is derived for the validity of a perturbed wave function of the form $\psi_0(1+\lambda v)$, where ψ_0 is the unperturbed wave function of the normal state and v the perturbing potential energy of a uniform electric field. It is also pointed out that inclusion of an electronic interaction term σ neglected by Kirkwood removes a difficulty appearing in his paper.

ACCORDING to dispersion theory,[1] if a uniform electric field vibrating sinusoidally with frequency ν is applied to an N-electron atom in the ground state 0, the polarizability (induced electric moment per unit field) is given by the equation:

$$\alpha = \frac{2e^2}{h} \sum_{n \neq 0} \frac{\nu_{n0} |z_{0n}|^2}{\nu_{n0}^2 - \nu^2}$$

where the direction of the electric field is taken as the z-axis, $z = \sum_{\mu=1}^{N} z_\mu$ (where z_μ refers to the μth electron),

$$\nu_{n0} = (W_n - W_0)/h , \quad z_{0n} = \int \bar{\psi}_0 z \psi_n d\tau ,$$

(matrix elements referred to unperturbed wave functions), and the summation is extended over all the excited states n, continous included. For a static field ($\nu = 0$), this becomes:

$$\alpha = 2e^2 \sum_{n \neq 0} \frac{|z_{0n}|^2}{W_n - W_0} . \tag{1}$$

Let us denote this summation by $\sum'$, and abbreviate $W_n - W_0$ to W_{n0}. In order to evaluate this sum, it is necessary to find a suitable center of gravity of the term system W_{n0}. We may define the proper average $\tilde{W}_{n0}$ by the equation

$$\tilde{W}_{n0} \sum' = \sum_{n \neq 0} |z_{0n}|^2,$$

but by the rule for a matrix product,

$$\sum_{n \neq 0} |z_{0n}|^2 = (z^2)_{00} - |z_{00}|^2 .$$

[1] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, p. 362, Eq. (31) (Oxford 1932).

Thus

$$\widetilde{W}_{n0} \sum{}' = (z^2)_{00} - |z_{00}|^2.$$

We may define another average $W_{n0}{}^*$ by the equation

$$W_{n0}{}^* \sum_{n \neq 0} |z_{0n}|^2 = \sum_{n} W_{n0} |z_{0n}|^2,$$

which by the Kuhn-Reiche sum rule equals $(h^2/8\pi^2 m)N$. Since ez_{00} denotes the electric moment averaged with respect to the wave function of the normal state unperturbed by the electric field, it must vanish, since experimentally no atoms have permanent dipole moments. One can also show[2] this by writing z_{00} as $\int |\psi_0|^2 z d\tau$ and applying the transformation $z_\mu' = -z_\mu$, whereupon $\psi_0(z) = \pm \psi_0(z')$, from which $z_{00} = -z_{00}$ and therefore vanishes. Thus

$$\sum_{n \neq 0} |z_{0n}|^2 = \sum_{n} |z_{0n}|^2 = (z^2)_{00},$$

so that

$$W_{n0}{}^* = (h^2/8\pi^2 n)N/(z^2)_{00}.$$

If we now take as an approximation $\widetilde{W}_{n0} = W_{n0}{}^*$, we find:

$$\sum{}' = (8\pi^2 m/h^2)[(z^2)_{00}]^2/N. \tag{2}$$

Now

$$(z^2)_{00} = \sum_{i} \sum_{j} (z_i z_j)_{00} = \sum_{i=1}^{N} (z_i^2)_{00} + \sum_{i \neq j} \sum (z_i z_j)_{00}$$

and

$$(z_i^2)_{00} = (x_i^2)_{00} = (y_i^2)_{00},$$

since these are averages with respect to the unperturbed wave function, in which the z direction is not favored; thus

$$(z_i^2)_{00} = \tfrac{1}{3}(x_i^2 + y_i^2 + z_i^2)_{00} = \tfrac{1}{3}(r_i^2)_{00}.$$

Similarly

$$(z_i z_j)_{00} = \tfrac{1}{3}(\vec{R}_i \cdot \vec{R}_j)_{00},$$

so that

$$(z^2)_{00} = \tfrac{1}{3} \sum_{i} (r_i^2)_{00} + \tfrac{1}{3} \sum_{i \neq j} \sum (\vec{R}_i \cdot \vec{R}_j)_{00}. \tag{3}$$

Let us denote

$$\sum_{i \neq j} \sum (\vec{R}_i \cdot \vec{R}_j)_{00}$$

by σ, and recall that for a monatomic gas, the molal diamagnetic susceptibility[3] is given by

$$\chi = -\frac{e^2 L}{6mc^2} \sum_{i=1}^{N} (r_i^2)_{00}, \tag{4}$$

[2] J. H. Van Vleck, reference 1, p. 202.
[3] J. H. Van Vleck, reference 1, p. 206, Eq. (2).

where L is Avogadro's number. Then, using Eqs. (1), (2), (3), and (4),

$$\alpha = \frac{16\pi^2 e^2 m}{9h^2 N}\left(\frac{6mc^2}{e^2 L}\,|\,\chi\,|\,+\,\sigma\right)^2. \tag{5}$$

We have here an approximate relation between the polarizability and the diamagnetic susceptibility of a monatomic gas, which can be tested only for the inert gases, since almost all others have strong paramagnetic susceptibilities which greatly outweigh the diamagnetic part. Since electrons repel each other, the average angle between two of the radius vectors R_i and R_j in an atom is expected to be greater than $\pi/2$, thus making σ a negative number. Actual calculation for helium using a wave function due to Hylleraas which gives the energy correct to one part in 3000, gave for σ the value $-0.146\ a_0^2$, so that σ is small compared to $(6mc^2/e^2 L)\,|\,\chi\,|=\sum_i(r_i^2)_{00}=+2.34\ a_0^2$ for helium. For neon σ was calculated by means of Slater's theory of complex spectra, using hydrogenic radial functions (with screening) for $1s$, $2s$, $2p$, giving a value of the order $-1.5\ a_0^2$; this is also small compared to $\sum_i(r_i^2)_{00}$ $=8.31\ a_0^2$ for neon.

We can rewrite (5) in the form:

$$|\,\chi\,| = (e^2 a_0^{1/2}/4mc^2)(N\alpha)^{1/2} - (e^2 L/6mc^2)\sigma. \tag{6}$$

We can now test this equation by calculating $|\,\chi\,|$ from the observed polarizability, and comparing with the observed $|\,\chi\,|$. We get the Table I.

TABLE I. *In this table K is the volume susceptibility reduced to 20°C and 1 atmos.* $=K_{20}=(\rho_{20}/M)\chi$, *where ρ is the density and M the atomic weight.*

	N	$10^{24}\alpha$ (obs.)	$10^6\,\vert K\vert$ (calc.)	$10^6\,\vert K\vert$ (obs.)
He	2	0.205	0.000088	0.000078
A	10	0.390	0.00031	0.00028

The law (6), with σ placed equal to zero, has been derived by Kirkwood,[4] using a method quite different formally from ours, so that it is of interest to show the equivalence of his assumptions to ours. Letting ψ_0 be the wave function of the normal state and $v = -eF\sum_1^N z_\mu$ the perturbing potential energy due to a uniform electric field of strength F, he writes an approximate wave function for the perturbed atom in the form $\psi_0(1+\lambda v)$, where λ is a parameter which he determines by minimizing the energy $\int\bar\psi H\psi d\tau$. Using the fact that v_{00} vanishes, the energy turns out after variation to be W_0 plus a second order term $-(\frac{1}{2})\alpha F^2$, where $\alpha = (8\pi^2 m/h^2)\,[(z^2)_{00}]^2/N$. He thus gets a formula for the polarizability which checks with ours except for the fact that he arbitrarily neglects [5]σ. If one makes use of the theorem that such a variational method applied to the lowest state of an atom must always give an

[4] J. G. Kirkwood, Phys. Zeits. **33**, 57 (1932).

[5] Kirkwood does not take his z-axis parallel to the field, but one can verify that on doing so, his method does lead directly to our Eq. (5). He places $\sigma=0$ by writing $\Theta_x=\sum_{j=1}^N(x_j^2)_{00}$ instead of $\Theta_x=\sum_j\sum_k(x_jx_k)_{00}$.

energy higher than the true energy, one sees that the calculated $|K|$ should be larger than the true $|K|$ in all cases. Kirkwood finds $|K|$ (calc.) for neon and argon less than $|K|$ (obs.), contrary to expectation; this is to be explained by his neglect of the interaction term σ.

Now the perturbed wave function which leads to the formula (1) for polarizability is that deducible from first-order perturbation theory:

$$\psi = \psi_0 + \sum_{j \neq 0}(v_{j0}/W_{0j})\psi_j. \tag{7}$$

If we make the assumption that

$$\sum_{j \neq 0}(v_{j0}/W_{0j})\psi_j = \lambda_a v \psi_0 \tag{8}$$

(where λ_a is the adjusted value of λ), our wave function checks with Kirkwood's and will thus give the same second order energy and the same polarizability. Eq. (8), however, on multiplication by $\bar{\psi}_0 v$ and integration over the electron coördinates leads (using Kirkwood's $\lambda_a = -(8\pi^2 m/h^2)(v^2)_{00}/(e^2 F^2 N)$), to

$$\sum_{j \neq 0} \frac{v_{j0}v_{0j}}{W_{0j}} = \lambda_a(v^2)_{00} = -\frac{8\pi^2 m\left[(v^2)_{00}\right]^2}{h^2 e^2 F^2 N}.$$

Using $v = -eFz$, this becomes

$$\sum_{j \neq 0} |z_{0j}|^2/W_{j0} = (8\pi^2 m/h^2 N)\left[(z^2)_{00}\right]^2,$$

or, using the Kuhn-Reiche sum rule,

$$\sum_{j \neq 0} \frac{|z_{0j}|^2}{W_{j0}} = \frac{\left[(z^2)_{00}\right]^2}{\sum_j W_{j0}|z_{0j}|^2}. \tag{9}$$

This, however, is just the assumption $\tilde{W}_{n0} = W_{n0}{}^*$ of our method. Thus the assumption (8) that leads to Kirkwood's treatment also leads to our assumption as to averages. Eq. (9) can be written:

$$\frac{\sum_{j \neq 0}|z_{0j}|^2/W_{j0}}{\sum_j |z_{0j}|^2} = \frac{\sum_j |z_{0j}|^2}{\sum_j W_{j0}|z_{0j}|^2}. \tag{10}$$

That is, the average (formed with respect to the squared matrix elements) of the reciprocal of W_{j0} must equal the reciprocal of the average of W_{j0}, in order that $\psi = \psi_0(1 + \lambda v)$. The accuracy of fulfilment of this relation thus constitutes a criterion for the accuracy of a perturbed wave function of the form $\psi_0(1 + \lambda v)$. Eq. (10) is seen to work well when $|z_{01}|^2 \gg |z_{02}|^2$ etc., with the $|z_{0j}|^2$ falling off rapidly. It is thus expected to work well in the case of the alkali vapors, since the first absorption line is very strong compared to the succeeding ones; unfortunately, however, these vapors are paramagnetic, so

that comparison with experiment is impossible. For the alkaline earth vapors (ground state $^1S_0$), there is no paramagnetism, but also no susceptibility measurements. Since they have no permanent magnetic moment, however, the Zeeman effect would be a measure of the magnetic polarizability. One should thus be able to use the law (6) to predict qualitatively second order Zeeman effect of the normal state from refractive index data or vice versa.

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