THE DIAMAGNETIC SUSCEPTIBILITY OF HYDROGEN MOLECULE AND OF HELIUM IN THE NEW QUANTUM MECHANICS

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In a paper by Van Vleck that appeared in these PROCEEDINGS,[1] a formula for the diamagnetic susceptibility of atoms and molecules in the new quantum mechanics was found which replaces Pauli's formula in the classical quantum theory. It gives the molar diamagnetic susceptibility

$$X_M = -(e^2L/6\mu c^2)\sum \overline{r^2} \tag{1}$$

where $\overline{r^2}$ is the time average of r^2 for one electron, or a diagonal element in the matrix for r^2; the summation extends over all electrons in an atom or a molecule.

In a recent paper by the author,[2] the hydrogen molecule problem was investigated by following the line of the Ritz method of solving variational problems. The function finally decided upon to approximate the solution of the wave equation for the normal hydrogen molecule is of the form

$$\psi = A\left[e^{-\frac{1.166(r_1+p_2)}{a}} + e^{-\frac{1.166(r_2+p_1)}{a}}\right] \tag{2}$$

where a = radius of 1_1 orbit, r_1 and p_1 are the distances of one of the electrons to the two nuclei, r_2 and p_2 those of the other electron and A is the constant of normalization. It was also found that when the potential energy of the molecule is a minimum the separation between the nuclei is $D = 1.406a$. In fact this equilibrium configuration is identified as the normal hydrogen molecule.

With these data given, we proceed to evaluate X_M for the molecule. The quantity r^2 in Van Vleck's formula is here evidently the square of the median from one of the electrons to the mid-point between the nuclei. Calling these two squares M_1^2 and M_2^2 for the two electrons, we have

$$\sum \overline{r^2} = \int (M_1^2 + M_2^2)\psi^2\, dV_1\, dV_2 \tag{3}$$

where $dV_1 = r_1^2 \sin\theta_1\, dr_1\, d\vartheta_1\, d\varphi_1$ and similar expressions for dV_2. Besides, we have the relations

$$M_1^2 = (r_1^2 + p_1^2)/2 - D^2/4, \qquad M_2^2 = (\gamma_2^2 + p_2^2)/2 - D^2/4. \tag{4}$$

After we introduce (2) and (4) into (3), the latter integrates explicitly into

$$\sum \overline{r^2} = \frac{2A^2\pi^2a^2}{(2 \times 1.166)^8} [1536 + 64Q^2 + 4e^{-Q}(Q^2 + 6Q + 12)(Q^5/5 +$$

$$2Q^4 + 12Q^3 + 48Q^2 + 144Q + 288)/3Q] - D^2/2$$

where $Q = 1.166 \times 2D$. For $D = 1.406a$, we get

$$\sum \overline{r^2} = 5.90 \ a^2 \quad \text{and} \quad X_M = -4.71 \times 10^{-6}.$$

Similar calculations of X_M have been made for the helium atom by utilizing the results of Kellner[3] who computed the energy value of helium according to the new quantum mechanics also by the Ritz method. The final approximative function has the form

$$\psi = e^{-\frac{\eta_1+\eta_2}{2}} [C_1L_1'(\eta_1)L_1'(\eta_2)P_0(x) + C_2L_1'(\eta_1)L_1'(\eta_2)P_1(x) +$$

$$C_3L_1'(\eta_1)L_1'(\eta_2)P_2(x) + C_4L_2'(\eta_1)L_2'(\eta_2)P_0(x)] \quad (5)$$

where $\eta_1 = 3.4 \ r_1/a$, $\eta_2 = 3.4 \ r_2/a$, $x = $ cosine of the angle between the two radii drawn from the nucleus to the electrons; the functions $L_n'(\eta)$ and $P_m(x)$ have their usual meanings. The energy value was calculated without actually determining the C's. In order to find $\sum \overline{r^2}$, it becomes necessary, however, to evaluate them. Using the energy value and other data given by Kellner, we obtain the following:

$$C_1 = 14.336/a^3 \qquad\qquad C_2 = -0.832/a^3$$
$$C_3 = -0.082/a^3 \qquad\qquad C_4 = -0.113/a^3$$

Putting these values of C's into (5) and carrying out the integration, we find

$$\sum \overline{r^2} = 1.917 \ a^2 \quad \text{and} \quad X_M - 1.53 \times 10^{-6}.$$

Experimental determinations of X_M for helium have been made by Wills and Hector[4] and those for hydrogen by Wills and Hector,[4] Soné[5] and Lehrer.[6] We tabulate below their experimental values as well as the calculated ones:

	CALCULATED	OBSERVED	
He	-1.53×10^{-6}	-1.88×10^{-6}	W. and H.
		$\begin{cases} -3.94 \times 10^{-6} \\ -3.99 \times 10^{-6} \\ -5.1 \ \times 10^{-6} \end{cases}$	W. and H.
H$_2$	-4.71×10^{-6}		Soné
			Lehrer

The energy values found by applying Ritz method to the approximate ψ-functions used above agree with the spectroscopic determinations to 0.9% in the case of helium and to about 2% in the case of hydrogen molecule. If we assume that these percentage errors just represent the discrepancies between the approximate and the exact "Eigenwerte" of the wave equations, the errors in the $\sum \overline{r^2}$ obtained above may still be much higher because the error in the ψ-functions are probably higher. This

follows from the fact that when we look at the wave equation from the calculus of variations standpoint, we know that in the neighborhood of the correct "Eigenfunktion" ψ and the correct "Eigenwerte" E, $\delta E = 0$ for any $\delta\psi$. Incidentally, this also indicates why the Ritz method seems to be a particularly powerful one in calculating the approximate energy values of the wave equation.

[1] Van Vleck, J. H., *Proc. Nat. Acad. Sci.*, **12**, 662, 1926.

[2] An abstract of this paper has appeared in the Bulletins of *Amer. Phys. Soc.*, Chicago meeting, November, 1927.

[3] Kellner, G. W., *Zeits. Physik*, **44**, 91, 1927.

[4] Wills and Hector, *Physic. Rev.*, **23**, 209, 1926; Hector, *ibid.*, **24**, 418, 1926.

[5] Soné, T., *Phil. Mag.*, **39**, 305, 1920.

[6] Lehrer, E., *Ann. Physik*, **81**, 229, 1926.

ON THE QUANTUM THEORY OF THE POLARIZATION OF IMPACT RADIATION

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The general theory of the polarization of light excited by electronic impact has been given in a previous paper.[1] In particular, it is shown that the polarization computed on the quantum mechanics is independent of the axis chosen for describing the directional degeneracy of the atom. It is further shown that, if one neglects the spin of the impacting electron and if one assumes that the perturbing interaction energy is small, the polarization of the emitted light may be computed "as if" only those states were excited, for which the component of angular momentum in a certain direction is the same as in the normal state; and the direction is that of the vector difference of the velocities of the incident and scattered electron. If this result is applied to electrons with just the necessary energy to excite the atom, it yields the momentum rule formulated by Skinner; the excitation does not change the component of angular momentum in the direction of the electron beam. Experimentally[2] one finds that these rules fail in two ways: (1) They do not apply to intercombination lines; in particular, they fail conspicuously for radiation from the $^3S_1$ and $^3P_1$ states of mercury; and (2) the observed polarization tends, as the energy of the exciting electron is diminished, first, towards a maximum, which in the case of normal lines is proportional to and of the same sign as that given by the rule, and, as the energy is further decreased, tends to zero. In this paper we shall show that the first of these discrepancies