

DIAMAGNETIC SUSCEPTIBILITY OF PERTURBED SYSTEMS

By

E. KAPUY

RESEARCH GROUP FOR THEORETICAL PHYSICS OF THE HUNGARIAN ACADEMY OF SCIENCES, BUDAPEST

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It is known that the computed value of the diamagnetic susceptibility is very sensitive to the wave function chosen for the calculation. Recently the exact eigenfunction of some states of the HeH^{2+} ion was determined for many different nuclear distances by BATES and CARSON [1]. The $1s\sigma$ ground state of HeH^{2+} can be considered as the simplest model of a perturbed system.

If the high-frequency paramagnetism [2] is to be calculated with the aid of perturbation calculations, then the eigenfunctions of all the excited states of HeH^{2+} are needed. These, however, are not at our disposal. Therefore it is advisable to apply the variation method, which has been derived by TILLIEU [3] for the calculation of the magnetic susceptibility of systems having zero resultant electronic angular and spin momentum. (In our case the spin momentum is equal to $\frac{\hbar}{2}$, however, this is disregarded, because we are interested only in the diamagnetic susceptibility.)

According to TILLIEU the χ_{ij} component of the susceptibility tensor is:

$$\chi_{ij} = -\frac{e^2}{4mc^2} \int \psi_0 [r^2 \delta_{ij} - x_i x_j] \psi_0 d\tau - \frac{e}{mc} \int \psi_0 [g_i L_j + g_j L_i] \psi_0 d\tau + \frac{\hbar}{m} \int \psi_0 [(\nabla g_i) (\nabla g_j)] \psi_0 d\tau. \quad (1)$$

Here by indices $i, j=1, 2, 3$ the coordinates x, y, z are denoted (for instance $\chi_{11} = \chi_{xx}$, $L_1 = L_x = \frac{\hbar}{i} \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$, $x_1 = x$, $x_2 = y$, $x_3 = z$), whereas ψ_0 is the wave function of the ground state of the system. The pure imaginary functions $g_i (i = x, y, z)$ are the solutions of the following differential equations:

$$\frac{\hbar^2}{2m} \psi_0 \Delta g_i + \frac{\hbar^2}{m} (\nabla \psi_0) (\nabla g_i) = -\frac{e}{2mc} L_i \psi_0, \quad (i = x, y, z). \quad (2)$$

Instead of the solution of the differential equation (1) such functions $g'_i = iG_i$ are chosen, which contain the variational parameters C_1, C_2, \dots, C_k

and which conform to the symmetry required by equation (2). After that the components χ_{ij} are calculated with the functions G_i ($i = x, y, z$) and the C_k -s are determined so that the χ_{ij} -s be maxima. (The susceptibility can namely be expressed with the aid of the energy: $\sum_{i=1}^3 \sum_{j=1}^3 \chi_{ij} \xi_i \xi_j = 2E(0) - 2E(\xi)$, here ξ is the magnetic field strength. $E(\xi)$ and $E(0)$ the energy of the system in a magnetic field of field strength ξ and without field, resp.).

He H^{2+} has $C_{\infty v}$ symmetry. The center of the coordinate system be in the nucleus He^{2+} , and the z axis be directed towards the nucleus H^+ . From $L_z \psi_0 = 0$ follow $G_z = 0$ and

$$\chi_{zz} = -\frac{e^2}{4mc^2} \int \psi_0 [x^2 + y^2] \psi_0 d\tau.$$

Since the problem is cylindrically symmetric :

$$\begin{aligned} \chi_{xx} = \chi_{yy} = & -\frac{e^2}{4mc^2} \int \psi_0 [y^2 + z^2] \psi_0 d\tau - \frac{2ie}{mc} \int \psi_0 G_x L_x \psi_0 d\tau - \\ & - \frac{\hbar^2}{m} \int \psi_0 |\nabla G_x|^2 \psi_0 d\tau, \end{aligned}$$

and the off-diagonal elements are equal to zero.

For the G_x -s the following expressions were chosen :

a) one-parameter expression : $G_x^{(a)} = Cy$,

b) two-parameter expression : $G_x^{(b)} = C_1 y + C_2 yz$.

In both cases the calculation of the integrals is equivalent to the determination of the mean values \bar{z} , \bar{z}^2 , \bar{x}^2 , \bar{y}^2 . These, however, can be readily found in the literature for the ground state of HeH^{2+} [4].

In the following Table the average molar susceptibilities

$$\chi_{mol} = \frac{\chi_{xx} + \chi_{yy} + \chi_{zz}}{3} N$$

are to be found (N is Avogadro's number), namely separately the so-called Langevin term χ_{mol}^L :

$$\chi_{mol}^L = -\frac{Ne^2}{6mc^2} \int \psi_0 r^2 \psi_0 d\tau,$$

the high-frequency term χ_{mol}^{HF}

$$\chi_{mol}^{HF} = -\frac{4ieN}{3mc} \int \psi_0 G_x L_x \psi_0 d\tau - \frac{2}{3} \frac{N\hbar^2}{m} \int \psi_0 |\nabla G_x|^2 \psi_0 d\tau$$

and the sum of both :

$$\chi_{mol} = \chi_{mol}^L + \chi_{mol}^{HF}$$

in electromagnetic units. (The quantities calculated with the one-parameter function $G_x^{(a)}$, and the two-parameter function $G_x^{(b)}$ are denoted by $\chi_{mol}^{HF(a)}$, $\chi_{mol}^{(a)}$ and $\chi_{mol}^{HF(b)}$, $\chi_{mol}^{(b)}$ resp.)

Table

R in a. u.	$\chi_{mol}^L \cdot 10^6$ in e. m. u.	$\chi_{mol}^{HF(a)} \cdot 10^6$ in e. m. u.	$\chi_{mol}^{(a)} \cdot 10^6$ in e. m. u.	$\chi_{mol}^{HF(b)} \cdot 10^6$ in e. m. u.	$\chi_{mol}^{(b)} \cdot 10^6$ in e. m. u.
0,0	-0,263	+0,000	-0,263	+0,000	-0,263
0,5	-0,399	+0,015	-0,384	+0,016	-0,383
1,0	-0,551	+0,025	-0,526	+0,031	-0,520
2,0	-0,620	+0,006	-0,614	+0,009	-0,611
3,0	-0,600	+0,001	-0,599	+0,002	-0,598
4,0	-0,595	+0,000	-0,595	+0,000	-0,595
5,0	-0,593	+0,000	-0,593	+0,000	-0,593
∞	-0,593	+0,000	-0,593	+0,000	-0,593

If therefore the nucleus H^+ approaches He^+ from the infinite, then first of all the term χ_{mol}^L begins to increase (from $R = 4$), later also χ_{mol}^{HF} increases (from $R = 2$) and from $R = 1,5$ (about the threefold Bohr radius of He^+) χ_{mol} is already smaller than the susceptibility of He^+ . For $R = 0$, of course, χ_{mol} agrees with the susceptibility of Li^{2+} .

It is well known that the susceptibility of some diamagnetic substances (for instance water) increases suddenly at the melting point and then increases slowly with increasing temperature (in absolute value). This can be interpreted according to what has been said before in the following way :

Owing to the increasing disorder and the thermal expansion the distance between the groups perturbing each other increases, χ_{mol}^{HF} decreases and thus χ_{mol} increases.

REFERENCES

1. D. R. BATES and T. R. CARSON, Proc. Roy. Soc. A, **234**, 207, 1956.
2. J. H. VAN VLECK, The Theory of Electric and Magnetic Susceptibilities, Oxford, University Press 1932.
3. J. TILLIEU, Ann. de Phys., 13. série **2**, 471, 631, 1957.
4. B. L. MOISEWITSCH and A. L. STEWART, Proc. Phys. Soc. **69**, 480, 1956.