LETTERS

수소분자에 있어서 섭동법에 의한 편극율의 계산

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Calculation of the Polarizability of Hydrogen Molecule by the Perturbation Method

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A number of investigators have published the polarizability of hydrogen molecule calculated by the variation[1~3] and perturbation method.[4,5] The polarizability calculation of Ishigaree, *et al*,[6] by 11+10 terms and 11+9 terms James-Coolidge type wave functions gave the polarizability value of hydrogen molecule which is very close to the experimental value. The polarizability of hydrogen molecule is calculated in this work, using the perturbation method. The modified form of the first order correction term of wave equation was derived by Lennard-Jones, using quantum mechanical method[7].

$$\phi_i^{(1)} = [\mathscr{H}' - H_{ii}']\phi_i^0/E_i^0$$
$$+ \sum_j{}' \frac{H_{ji}'}{[E_i^0 - E_j^0]} E_i^0/E_i^0 \phi_j^0$$

where

$$H_{ii}' = E_i^{(1)} = \langle \phi_i^0 | \mathscr{H}' | \phi_i^0 \rangle \qquad (1)$$

Substituting the modified form of the first order correction term of the wave equation into the second order correction of energy leads to the modified form of the second order correction of energy.

$$E_i^{(2)} = \langle \phi_i^0 | [\mathscr{H}' - E_i^{(1)}] | \phi_i^{(1)} \rangle$$
$$= \sum{}' H_{ji}' H_{ij}' / [E_i^0 - E_j^0] \qquad (2)$$
$$E_i^{(2)} = \langle \phi_i^0 | \mathscr{H}'^2 | \phi_i^0 \rangle / E_i^0 - H_{ii}' / E_i^0$$
$$+ \sum{}'' H_{ji}' H_{ij}' E_j^0 / E_i^0 (E_i^0 - E_j^0) \qquad (3)$$

where $\mathscr{H}' = x, y$ or z and $H_{ij}' = \langle \phi_i^0 | \mathscr{H}' | \phi_j^0 \rangle$

The polarizability which is the induced electric moment per unit field is given by[8]

$$\alpha_q = -\lambda \langle \phi_i^0 | \mathscr{H}' | \phi^{(1)} \rangle / F$$
$$= -2e\lambda \sum{}' H_{ji}' H_{ij}' / [E_i^0 - E_j^0]$$
$$= -2e^2 E_i^{(2)} \qquad (4)$$

where

$$q = x, \ y \ \text{or} \ z$$

Substituting equation (3) into (4) gives the expression for the polarizability of the molecule.

$$\alpha_q = -2e^2 \{ \langle \phi_i^0 | \mathscr{H}'^2 | \phi_i^0 \rangle / E_i^0 - H_{ii}' / E_i^0$$
$$+ \sum{}' H_{ij}' H_{ji}' E_j^0 / E_i^0 [E_i^0 - E_j^0] \} \qquad (5)$$

Table 1. The polarizability of hydrogen molecule (10^{-25} cm³).

Excited state	α_{zz}			α_{xx}		
	This work	Eastrope	Expl. [13]	This work	Eastrope	Expl. [14]*
$(1s)^2, {}^2\Sigma$	8,720	5.43		4.962	5.14	·
$1s_\sigma, 2s_\sigma {}^1\Sigma_u$	0.700	0.59		—	—	
$1s_\sigma, 2p_\sigma {}^1\Sigma_u$	1.111	0.95		—	—	
$1s_\sigma, 2p_\pi {}^1\Pi_u$	—	—		1.287×2	0.42×2	
$1s_\sigma, 3s_\sigma {}^1\Sigma_u$	0.085	0.08		—	—	
$1s_\sigma, 3p_\sigma {}^1\Sigma_u$	0.234	0.18		—	—	
$1s_\sigma, 3p_\pi {}^1\Pi_u$	—	—		0.126×2	0.003×2	
Total	10.85	7.23	10.28	7.788	5.89	7.14
$\alpha_{/}-\alpha_{\perp}$	3.062	3.60		—	—	—
$\langle\alpha\rangle$	8.81		8.19	—	—	—

Following Mrowka[9], the Heitler–London wave functions are assumed to represent the ground state of the hydrogen molecule and following Eastrope, the important contributions to the polarizability of the hydrogen molecule are assumed to come from the following terms,

$$1s_\sigma, 2s_\sigma {}^1\Sigma_u \quad 1s_\sigma, 2p_\sigma {}^1\Sigma_u \quad 1s_\sigma, 2p_\pi {}^1\Pi_u(\text{double})$$
$$1s_\sigma, 3s_\sigma {}^1\Sigma_u \quad 1s_\sigma, 3p_\sigma {}^1\Sigma_u \quad 1s_\sigma, 3p_\pi {}^1\Pi_u(\text{double})$$

The wave functions which were derived by the method of Kemble and Zerner[10] were adopted to represent the above terms. The polarizability contributions from the above terms for the hydrogen molecule along the Z and Y axis were calculated, substituting the dipole moment matrix elements for those terms calculated by the expansion method for spherical harmonics[11,12]. The calculated polarizability tensor components for the hydrogen molecule are listed in Table 1 with Eastrope values and the experimental values.

As shown in Table 1, the calculated values in this work are closer to the experimental values than those of Eastrope. The above good results are due to an improvement of the calculation method compared to Eastrope's work.

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