A UAO Treatment of the van der Waals Force

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Dispersion forces for numerous molecules and atoms have been estimated by London's[1] and Slater-Kirkwood's[2] dispersion formula. However, the exact theoretical evaluation is nearly impossible to achieve except for the simplest molecules and atoms. Approximate formulas are usually used to estimate the magnitude of this force between them.

London's one-term approximation formula is written as:

$$\langle \varDelta E\rangle_{\mathrm{AV}} = -\frac{3}{2R^6}\,\frac{\varDelta_1\varDelta_2}{\varDelta_1+\varDelta_2}\,\alpha_1{}^0\alpha_2{}^0 \qquad (1)$$

Here the subscripts refer to the two different molecules, α^0 is the polarizability, and $\varDelta$ is taken to be equal to the ionization energies of the molecules.

In the present paper, non-empirical calculation is made on the dipole-dipole interaction term of dispersion force between two CH_4, $NH_4{}^+$ and H_2O molecules and two neon atoms by the perturbation theory. In the course of calculation, we make use of the UAO[3,4] (united atom approach or central field approximation) which was used to obtain ionization potential, dissociation energy and so on in simple molecules with nearly spherical configuration. By the UAO method, the total wave function for CH_4, $NH_4{}^+$ and H_2O which involves only three parameters is a ten-electron Slater determinant Φ with configuration $(1s)^2\ (2s)^2\ (2p)^6\ {}^1S$ as same as neon atom. The one electron wave function of each molecule and atom is as follows:

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[1] F. London, *Trans. Faraday Soc.*, **33**, 8 (1937).

[2] J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 682 (1931).

[3] K. Funabashi and J. L. Magee, *J. Chem. Phys.*, **26**, 407 (1957).

[4] M. J. M. Bernal, *Proc. Phys. Soc.*, **A66**, 514 (1953).

TABLE I. DISPERSION FORCE. THE VALUES OF THE COEFFICIENT OF R^{-6} TERM (IN UNITS OF 10^{-60} erg. cm^6)

	Ne	NH_4^+	CH_4		H_2O	
			1	2	1	2
α	9.7	6.71	5.01	5.18	7.1648	7.3551
β	5.86	2.17	5.01	5.18	7.1648	7.3551
γ	5.86	1.62	3.00	2.59	3.5824	2.9420
Our results	5.75	153.9	181.5	375.4	112.7	278.4
In Margenau's table⁵⁾	7.97 7.48 4.67	(107.9)	112		47	
Estimated by second virial coefficient⁶⁾	8.32	—	240		—	
E_{AV}*	51.4	25**	28.2		25.6	

* The values of E_{AV} adopted in this paper are the same as those in Margenau's paper⁵⁾.

** The value of ionization potential is roughly estimated from those of NH_3 and CH_4, and α^0 is 2.68×10^{-24} cm^3 estimated from atomic refractive indexes.

For CH_4 and H_2O molecules³⁾

$$\varphi_{1s}=\left(\frac{\alpha^3}{\pi}\right)^{1/2}e^{-\alpha r}$$

$$\varphi_{2s}=\frac{1}{4}\left(\frac{\beta^3}{2\pi}\right)^{1/2}(2-\beta r)e^{-(\beta/2)r}$$

$$\left.\begin{matrix}\varphi_{2px}\\ \varphi_{2py}\\ \varphi_{2pz}\end{matrix}\right\}=\left(\frac{\gamma^5}{32\pi}\right)^{1/2}r\,e^{-(\gamma/2)r}\left\{\begin{matrix}\sin\theta\cos\varphi\\ \sin\theta\sin\varphi\\ \cos\theta\end{matrix}\right.$$

For NH_4^+ ion, the radial factors are⁴⁾

$$R_{1s}=(2\alpha)^{3/2}e^{-\alpha r}$$

$$R_{2s}=\left\{\frac{12\beta^5}{\alpha^2-\alpha\beta+\beta^2}\right\}^{1/2}\left\{1-\frac{1}{3}(\alpha+\beta)r\right\}e^{-\beta r}$$

$$R_{2p}=\left(\frac{4\gamma^5}{3}\right)^{1/2}r\,e^{-\gamma r}$$

As to the neon atom, we use the Slater orbitals, and the effective nuclear charge in each orbital is calculated by Slater's rule.

The values of the three parameters adopted are the same as in the quoted papers, and they aer listed in Table I.

The unperturbed total wave function Φ can be written as $\Phi=\Phi_1\cdot\Phi_2$, since the exchange of electrons does not occur in the range where the intermolecular distance between molecules (or atoms) 1 and 2 is very great.

The potential due to the dipole-dipole interaction between to molecules (or atoms) is given as follows:

$$V=\frac{e^2}{R^3}\sum_{i,j}(x_{1i}x_{2j}+y_{1i}y_{2j}-2z_{1i}z_{2j}) \tag{2}$$

where R is the distance between molecules or atoms, and x_{1i}, y_{2j} are the x and y coordinates for ith and jth electrons belonging to molecules (or atoms) 1 and 2, respectively. The z-axes are taken along the intermolecular distance R.

Taking the interaction V as a perturbation, the perturbation energy between the same molecules (or atoms) is given by

$$\varDelta E=(00|V|00)+\sum_{k_1,k_2}\frac{|(00|V|k_1k_2)|^2}{2E(0)-E(k_1)-E(k_2)} \tag{3}$$

where index 0 refers to the state function of the ground state, k referring to all possible excited states.

In the above equation, it can be shown that $(00|V|00)$ is zero in the present treatment. In the second term, if one replaces the dominator of Eq. 3 by a mean E_{AV}, the second order perturbation energy can be

$$\varDelta E=\frac{1}{E_{AV}}\sum_{k_1,k_2}|(00|V|k_1k_2)|^2=\frac{(00|V^2|00)}{E_{AV}} \tag{4}$$

E_{AV} is put equal to twice the ionization potential according to the treatment of Margenau⁵⁾.

Thus, $\varDelta E$ is calculated as follows:

$$\varDelta E=-\frac{24e^4}{R^6E_{AV}}\Big[\frac{1}{3}(1s|r^2|1s)+\frac{1}{3}(2s|r^2|2s)+(2p_\sigma|z^2|2p_\sigma)+2(2p_\pi|z^2|2p_\pi)-2(1s|z|2p_\sigma)^2-2(2s|z|2p_\sigma)^2\Big]^2 \tag{5}$$

where $2p_\pi$ refers to φ_{2px} or φ_{2py} and $2p_\sigma$ is to φ_{2pz}, and

$$(1s|r^2|1s)=\int\varphi_{1s}{}^*r^2\varphi_{1s}\,d\tau$$

$$(2p_\sigma|z^2|2p_\sigma)=\int\varphi_{2pz}{}^*z^2\varphi_{2pz}\,d\tau$$

The numerical values of the coefficient of

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5) H. Margenau, *Rev. Modern Phys.*, **11**, 1 (1939).

R^{-6} term in ΔE of the present molecules and atoms are listed in Table I.

As to methane and neon with uniformly charged spherical configuration, the values of the coefficient of R^{-6} term in ΔE almost agree with those calculated by London's approximate formula and also with those estimated by the second virial coefficient[6]. But, for H_2O, the value of the coefficient of R^{-6} term in ΔE is greater than the one obtained by London's formula, since the H_2O molecule belongs to C_{2v} and its UAO treatment may be inadequate.

Two kinds of calculations referring respectively to case 1 and case 2, are made, in which three different parameters are adopted for wave functions. The results indicate that the values of the coefficient of ΔE depend greatly on the values of parameters, in particular, on those of the outermost shell orbital. For example, the calculated values in H_2O in case 1 is three times as great as those in case 2. However, it may be remarked that the modification of these parameters in cases 1 and 2 causes a change of only less than 1% in the total electronic energy[3].

In regard to NH_4^+, R^{-6} term in interaction energy is of minor importance, since this molecule is an ion. However, in a rough estimation of this term by Eq. 1, the coefficient of R^{-6} term becomes 107.9. Hence, the calculated values seem to be reasonable.

The UAO procedure will also be applicable to SiH_4[7], PH_3 and other molecules which have at least a nearly spherical symmetry. This point will be investigated in future.

Our conclusion is as follows:

1) The UAO calculation of intermolecular interaction energy due to dipole-dipole is rather simple and easy, while the agreement is comparatively good.

2) Care must be taken, however, when one treats the molecule which deviates to a great extent from spherical symmetry.

3) The parameter dependence of the interaction energy is greater than that of the electronic energy of a molecule.

4) Therefore, to adopt better parameters is most important in carrying out the calculation by the UAO method. For this purpose, attention should be paid to the polarization which may take place when two molecules come near each other.

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[6] M. Mizushima, "Bunshiron", Kyoritu, Tokyo (1950), p. 270.

[7] C. Carter, *Proc. Roy. Soc.* (*London*), A235, 321 (1956).