Intermolecular Force Field of Linear Molecules with Quadrupole Moments

A. D. Buckingham

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A. D. BUCKINGHAM
Department of Theoretical Chemistry, University of Cambridge, England
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POPLE[1] showed that the second virial coefficient of an assembly of axially symmetric molecules, the interaction energy u_{12} of any two of them, distant r apart, being

$$u_{12}=4\epsilon\left\{\left(\frac{r_0}{r}\right)^{12}-\left(\frac{r_0}{r}\right)^{6}\right\}+\text{quadrupole}-\text{quadrupole energy}, \quad (1)$$

where ϵ and r_0 are parameters having the dimensions of energy, and length is given by

$$B(T)=\frac{2\pi Nr_0^3}{3}\left\{F(y)-\frac{7}{320}\left(\frac{\Theta^2}{\epsilon r_0^5}\right)^2 H_{10}(y)+\cdots\right\}, \quad (2)$$

where

$$y=2\left(\frac{\epsilon}{kT}\right)^{\frac12}, \quad F(y)=-\frac{y^{\frac12}}{4}\sum_{p=0}^{\infty}\Gamma\left(\frac{2p-1}{4}\right)\frac{y^p}{p!},$$

$$H_n(y)=y^{(27-n)/6}\sum_{p=0}^{\infty}\Gamma\left(\frac{6p+n-3}{12}\right)\frac{y^p}{p!}. \quad (3)$$

The quadrupole moment Θ is defined by $\Theta=\sum_i e_i(z_i^2-x_i^2)$ where z_i is measured along the axis, and x_i perpendicular to it. Subsequent terms in the expansion, which include both odd and even powers of $\Theta^2/\epsilon r_0^5$, are alternatively positive and negative, so make only a small contribution to $B(T)$ (see Buckingham and Pople[2]). Pople determined ϵ, r_0, and Θ by obtaining the best fit of the second virial data, and then compared the calculated heat of sublimation at absolute zero with the observed value. However, since the virial data can be fitted nearly as well by considerably

TABLE I. Calculated and experimental data for N_2 and CO_2.

Substance	E (cal/mole)	ϵ/k (°K)	r_0 (A)	$\Theta\times10^{26}$ (esu)		a_0 (A)	
				calc	from micro-wave data	calc	exptl
N_2	1800[a]	94	3.78	1.20	1.5[c]	4.09	4.00
CO_2	6530[b]	182.4	3.94	5.29	3.1[c]	4.07	3.92

[a] See reference 3.
[b] W. F. Giauque and C. J. Egan, J. Chem. Phys. 5, 45 (1937).
[c] Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), p. 1028.

different values of the parameters, a preferable procedure is to use a successive approximation method to determine $\Theta^2/\epsilon r_0^5$ so that the heat of sublimation is given precisely and to employ the second virial data to yield ϵ and r_0.

The heat of sublimation H, of a face centred cubic lattice of molecules interacting according to (1), at absolute zero, is related to the Debye temperature θ by (see Pople[1] and Lupton[3]).

$$H+\frac98 Nk\theta=E=2N\epsilon\left\{12.1318\left(\frac{r_0}{a}\right)^{12}-14.4539\left(\frac{r_0}{a}\right)^{6}\right.$$
$$\left.-5.3533\frac{\Theta^2}{\epsilon r_0^5}\left(\frac{r_0}{a}\right)^{5}\right\}, \quad (4)$$

TABLE II. Calculated and experimental second virial coefficients for N_2 and CO_2.

	N_2			CO_2	
T (°C)	$B(T)_{\text{exptl}}$[a] (cm³/mole)	$B(T)_{\text{calc}}$ (cm³/mole)	T (°C)	$B(T)_{\text{exptl}}$[b] (cm³/mole)	$B(T)_{\text{calc}}$ (cm³/mole)
0	−10.4	−10.2	0	−156.4	−147.3
25	−4.8	−4.5	50	−101.7	−102.3
50	−0.3	0.2	100	−71.9	−73.1
75	3.2	4.1	150	−51.6	−52.7
100	6.6	7.6	200	−34.3	−37.6
125	9.6	10.2	300	−13.3	−17.2
150	12.5	12.6	400	−2.0	−4.0
			500	6.0	5.1
			600	12.0	11.8

[a] Michels, Wouters, and de Boer, Physica 1, 587 (1934).
[b] K. E. MacCormack and W. G. Schneider, J. Chem. Phys. 18, 1269 (1950).

and E must be minimized with respect to a, yielding a_0, where a is the distance between nearest neighbors. The inclusion of quadrupole-induced dipole interactions would not affect E, owing to the symmetry of the lattice.

Lupton[2] performed somewhat similar calculations on N_2 and CO, but he employed ϵ and r_0 values computed from the second virial data using a Lennard-Jones potential only, and then adjusted the quadrupole moment to fit the observed E. A more consistent procedure is the one outlined above, and this was applied to N_2 and CO_2. The data and results are shown in Tables I and II.

[1] J. A. Pople, Proc. Roy. Soc. (London) A221, 508 (1954).
[2] A. D. Buckingham and J. A. Pople, Trans. Faraday Soc. (to be published).
[3] J. M. Lupton, Thesis (University of Amsterdam, 1954).

Applications of the Alternant Molecular Orbital Method to Six- and Four-Electron Systems

HIROYUKI YOSHIZUMI AND TAKASHI ITOH
Department of Physics, University of Tokyo, Tokyo, Japan
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IN many molecules and crystals the electronic wave function of the ground state is to the first approximation given by a single determinant constructed from molecular orbitals (or Bloch orbitals); each doubly occupied by electrons of opposite spins. The greatest shortcoming of such a determinantal wave function is found in its incapability of taking into account the correlation between the motions of electrons. It contains, however, some correlation between electrons of parallel spin introduced by the Pauli exclusion principle, but none for the antiparallel spin.

To remedy this defect one must carry out the extensive C.I. (configuration interaction) calculation. But the complete C.I. calculation becomes practically impossible for large systems.

Recently Löwdin proposed a new attack for the treatment of antiparallel spin using the alternant molecular orbital.[1,2] His method seems to present a powerful method by which the major part of the effect of C.I. can be taken into account. In this letter the applications of the method to benzene (six π electron system) and to acetylene (four π electron system) are reported.

(1) Benzene. The alternant MO are defined by

$$\phi_{II}=\cos\theta\phi_l+\sin\theta\phi_{l+3},$$
$$\phi_{III}=\cos\theta\phi_l-\sin\theta\phi_{l+3},$$

where

$$\phi_l(r)=(6\sigma_l)^{-\frac12}\sum_{k=1}^{6}\exp\left(\frac{2\pi ikl}{6}\right)\cdot U_k(r).$$

The I-type orbitals have large amplitudes on the alternant atoms (say 1,3,5), while the II-type orbitals on the other atoms (2,4,6). Using these orbitals, we construct the ground state wave function ($^1A_{1g}$),

$$\Psi_i(\theta)=N_i\sum_P (-1)^P P\phi_{0I}(1)\phi_{II}(2)\phi_{-II}(3)\phi_{0II}(4)\phi_{III}(5)\phi_{-III}(6)\cdot\chi_i,$$

where χ_i represents a singlet spin function. By adjusting θ to the optimum value, maximum depression of total energy is obtained, and this value is to be compared with the result of the C.I.

There are five singlets for six electron system,[3] and two of them are shown in Fig. 1.
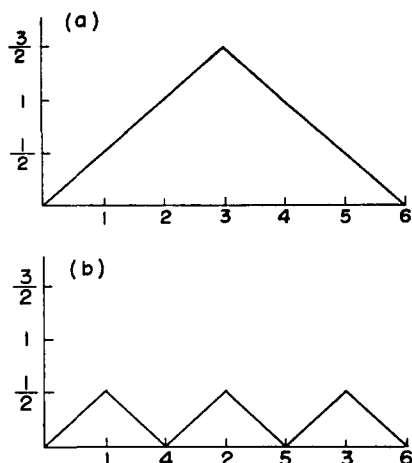
FIG. 1. Two types of spin coupling.

$$\chi_a = \alpha_1\alpha_2\alpha_3\beta_4\beta_5\beta_6$$
$$-\tfrac{1}{3}(\beta_1\alpha_2\alpha_3 + \alpha_1\beta_2\alpha_3 + \alpha_1\alpha_2\beta_3)(\alpha_4\beta_5\beta_6 + \beta_4\alpha_5\beta_6 + \beta_4\beta_5\alpha_6)$$
$$+\tfrac{1}{3}(\alpha_1\beta_2\beta_3 + \beta_1\alpha_2\beta_3 + \beta_1\beta_2\alpha_3)(\beta_4\alpha_5\alpha_6 + \alpha_4\beta_5\alpha_6 + \alpha_4\alpha_5\beta_6)$$
$$-\beta_1\beta_2\beta_3\alpha_4\alpha_5\alpha_6,$$

$$\chi_b = (\alpha_1\beta_4 - \beta_1\alpha_4)(\alpha_2\beta_5 - \beta_2\alpha_5)(\alpha_3\beta_6 - \beta_3\alpha_6).$$

Now, the type (a) coupling of Fig. 1 is expected to give a satiss factory result. When the type (a) coupling is adopted, the spin- of electrons in the same type (I or II) orbitals are added to the resultants $\tfrac{3}{2}$, and then the two resultants are added to singlet. Then $\Psi_a(\theta)$ contains the correlation effect of antiparallel spins through the alternant character of I- and II-type orbitals and that of parallel spins through the Pauli principle. The results of the calculation are shown in Fig. 2, which shows clearly the superiority of coupling (a). The energy depression for curve (a)
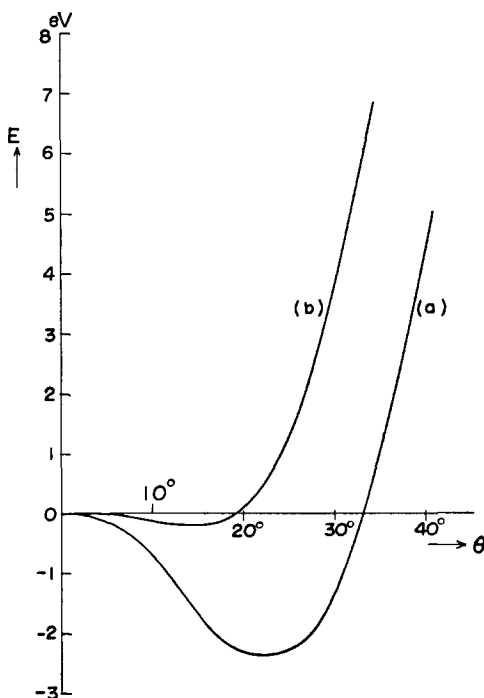

FIG. 2. Energy curves.

is 2.35 ev, which is 85 percent of the value obtained by the C.I. of nine $^1A_{1g}$ functions.[4]

(2) Acetylene. The same method is applied for acetylene as for benzene. The energy depression is about 70 percent of the complete C.I. calculation carried out by Nakamura et al.[5] Generally speaking the curves for this case show the similar tendency as in benzene case.

The full paper for benzene will be published shortly in the Journal of the Physical Society of Japan, and the detailed results for acetylene including the applications for the excited states will be reported elsewhere.

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[1] P. O. Löwdin, "Symposium on molecular physics," Nikko, Japan (1953).
[2] P. O. Löwdin, "Quarterly progress report," Solid-State and Molecular Theory Group, M.I.T., July 15, 1954, p. 22.
[3] G. W. Pratt, Jr., Phys. Rev. 92, 278 (1953).
[4] Parr, Craig, and Ross, J. Chem. Phys. 18, 1561 (1950).
[5] Nakamura, Ohno, Kotani, and Hijikata, Progr. Theoret. Phys. 8, 387 (1952).

Pure Rotational Absorption Spectrum of Hydrogen

J. A. A. KETELAAR, J. P. COLPA, AND F. N. HOOGE
Laboratory for General and Inorganic Chemistry of the University of Amsterdam, Amsterdam, The Netherlands
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IN the course of our investigations[1] on the infrared absorption spectra of gases and gas mixtures we observed that compressed hydrogen contrary to, e.g., nitrogen did show a remarkable absorption at wavelengths in the 8μ to 15μ region.

The observed extinction curves for hydrogen at pressures up to 114 atmospheres with an optical pathlength of 100 cm are reproduced in Fig. 1.

The extinction is very nearly proportional to the square of the pressure ($\simeq$density). The observed spectrum has to be ascribed to the pressure induced pure rotation spectrum of hydrogen. The shoulders are due respectively to the transitions $J=2\rightarrow J=4$ and $J=3\rightarrow J=5$; calculated at 813.9 cm^{-1} and 1034.1 cm^{-1} according to Herzberg[2] with the formula

$$F_{v=0}(J) = 59.300J(J+1) - 0.04581J^2(J+1)^2 + 0.0000518J^3(J+1)^3.$$
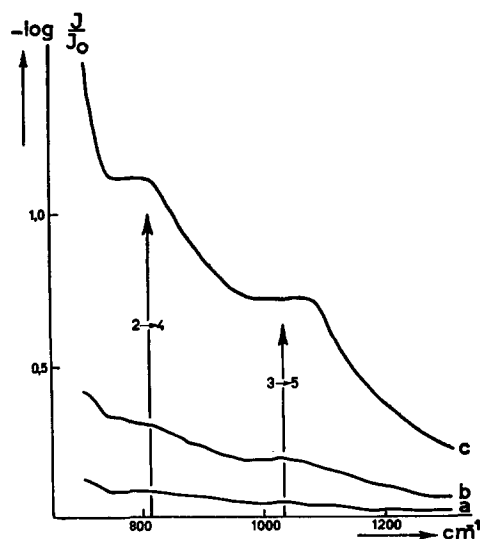

FIG. 1. Minus $\log I/I_0$ versus wave number for pure hydrogen, where a is 28.5 atmos, b is 57 atmos, and c is 114 atmos. The arrows indicate the calculated wave numbers of the transitions $J=2\rightarrow J=4$ and $J=3\rightarrow J=5$.