Interaction of the van der Waals Type Between Three Atoms

B. M. AXILROD AND E. TELLER
George Washington University, Washington, D. C.
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IT is recalled that the van der Waals attraction between atoms may be represented in good approximation by a sum of interactions between pairs of atoms.[1] This approximation is obtained by applying perturbation theory to the second order. The resulting interaction potential is of the order of $V\alpha/r^6$ where V is the ionization energy, α is their polarizability, and r is their distance.

If the perturbation calculation is pursued to the third order, interactions between triplets of atoms appear. The order of magnitude of the interaction is

$$\frac{V\alpha^3}{r_{12}^3 r_{23}^3 r_{31}^3},$$

where r_{12}, r_{23}, and r_{31} are the distances between the atoms. The magnitude and even the sign of the interaction potential depend upon the shape of the triangle with the sides r_{12}, r_{23}, and r_{31}. Our purpose is to investigate the character of this dependence.

The term in the third-order interaction energy which depends on triplets of atoms is

$$W_0''' = \sum_{\substack{l \\ l\neq 0}} \sum_{\substack{j\neq 0 \\ j\neq l}} \frac{H_{0j}H_{jl}H_{l0}}{(W_j - W_0)(W_l - W_0)},$$

where W_j, W_l, and W_0 are the unperturbed energies of the intermediate states j and l, and the ground state, respectively. In the numerator H_{0j}, etc., are matrix elements of the perturbation. As the perturbing potential we introduce dipole-dipole interactions between pairs of atoms. We further make the assumption that the lowest states of the interacting atoms are s states. Then in the state designated by subscript j and also in the state designated by subscript l two atoms will be in p levels. One of the three atoms is in the same p level in states j and l. Each of the other atoms is in the lowest s level in one of the states l or j and in a p level in the other of the states l or j.

The dependence of the perturbation potential on the shape of the triangle of the three atoms is due to two reasons. Firstly, the three matrix elements H_{0j}, H_{jl}, and H_{l0} contain the three factors, $1/r_{12}^3$, $1/r_{23}^3$, and $1/r_{31}^3$ (not necessarily in the order given). Secondly, the dipole-dipole interaction depends on the orientation of the interacting dipoles relative to each other and relative to the line connecting them. The orientation of a dipole depends on which particular substate of the degenerate p level was chosen. Subsequently one must carry out the summation over all the substates corresponding to the various p levels that can occur in intermediate states.

The summation can be carried out by a straightforward but lengthy calculation. One obtains

$$W_0''' = C\frac{3\cos\gamma_1\cos\gamma_2\cos\gamma_3 + 1}{r_{12}^3 r_{23}^3 r_{31}^3},$$

where γ_1 is included by the sides r_{12} and r_{31} with similar definitions for γ_2 and γ_3. C is a positive quantity of the order $V\alpha^3$. Its exact magnitude depends on the energies of p levels in the three atoms and on the magnitudes of the dipole matrix elements.

It is of interest to apply the equation to a few special configurations of atoms.

Case 1. *The equilateral triangle.* For $\gamma_1=\gamma_2=\gamma_3$ the interaction energy is

$$W_0''' = C\frac{11/8}{r_{12}^3 r_{23}^3 r_{31}^3}$$

which is positive, and hence the interaction is one of repulsion.

Case 2. *A right triangle.* For $\gamma_1=90°$ the interaction energy is

$$W_0''' = C\frac{1}{r_{12}^3 r_{23}^3 r_{31}^3}$$

and again the interaction is repulsive.

[1] Pauling and Wilson, *Introduction to Quantum Mechanics* (1935), Chap. XIV.

Case 3. *Three atoms in a line.* For $\gamma_1=\gamma_2=0$ and $\gamma_3=180°$ the interaction potential is

$$W_0'''=C\frac{-2}{r_{12}^3r_{23}^3r_{31}^3}$$

which indicates attraction.

Case 4. *One atom far removed from the other two.* For $r_{31}\gg r_{12}r_{31}\leqq r_{23}$ and $\gamma_3\leqq 0$ so that the interaction energy becomes

$$W_0=C\frac{(-3\cos^2\gamma_1+1)}{r_{31}^6r_{12}^3}.$$