Interaction of the van der Waals Type Between Three Atoms

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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. 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, $\alpha$ is its 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

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

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

$$W_0''' = \sum_{i,j,k} \sum_{(j \neq i) \neq (k \neq i) \neq (i \neq j)} \frac{H_0H_2H_0}{(W_j-W_0)(W_I-W_0)},$$

where $W_j$, $W_i$, and $W_0$ are the unperturbed energies of the intermediate states $j$ and $l$, and the ground state, respectively. In the numerator $H_0$, 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 $H_{0j}$, $H_{ji}$, and $H_{ij}$ 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

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

where $\gamma_1$ is included by the sides $r_{12}$ and $r_{31}$ with similar definitions for $\gamma_2$ and $\gamma_3$. $C$ 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

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

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

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

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

and again the interaction is repulsive.

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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 $\gamma_3 = 180^\circ$ the interaction potential is

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

which indicates attraction.

Case 4. *One atom far removed from the other two.* For $r_3 \gg r_{12}, r_{23}$ and $\gamma_3 \leq 0$ so that the interaction energy becomes

$$W_0 = C \frac{(-3 \cos^2 \gamma_1 + 1)}{r_{31}^6 r_{13}^3}.$$