

Van der Waals forces play an important role in physical chemistry, especially when the two atoms under consideration have no valence electrons (forces between rare gas atoms, stable molecules, etc.). They are partially responsible for the differences between the behavior of a real gas and that of an ideal gas. Finally, as we have already said, these are long-range forces, and are therefore involved in the stability of colloids.

We shall begin by determining the expression for the dipole-dipole interaction Hamiltonian between two neutral hydrogen atoms (§1). This will then enable us to study the Van der Waals forces between two atoms in the $1s$ state (§2), or between an atom in the $2p$ state and an atom in the $1s$ state (§3). Finally, we shall show (§4) that a hydrogen atom in the $1s$ state is attracted by its electrical mirror image in a perfectly conducting wall.

1. The electrostatic interaction Hamiltonian for two hydrogen atoms

a. NOTATION

The two protons of the two hydrogen atoms are assumed to remain motionless at points A and B (fig. 1). We shall set:

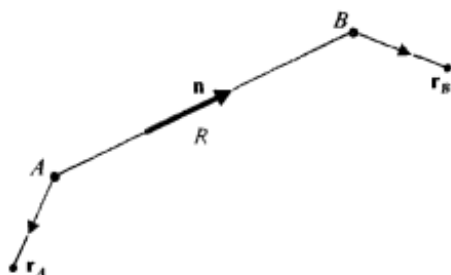


FIGURE 1

Relative position of the two hydrogen atoms. R is the distance between the two protons, which are situated at A and B , and \mathbf{n} is the unit vector on the line joining them. \mathbf{r}_A and \mathbf{r}_B are the position vectors of the two electrons with respect to points A and B respectively.

$$\mathbf{R} = \mathbf{OB} - \mathbf{OA} \quad (1)$$

$$R = |\mathbf{R}| \quad (2)$$

$$\mathbf{n} = \frac{\mathbf{R}}{|\mathbf{R}|} \quad (3)$$

R is the distance between the two atoms, and \mathbf{n} is the unit vector on the line which joins them. Let \mathbf{r}_A be the position vector of the electron attached to atom (A) with respect to point A , and \mathbf{r}_B , the position vector of the electron attached to atom B

with respect to B . We call :

$$\mathcal{D}_A = q \mathbf{r}_A \quad (4)$$

$$\mathcal{D}_B = q \mathbf{r}_B \quad (5)$$

the electric dipole moments of the two atoms (q is the electron charge).

We shall assume throughout this complement that :

$$R \gg |\mathbf{r}_A|, |\mathbf{r}_B| \quad (6)$$

Although they are identical, the electrons of the two atoms are well separated, and their wave functions do not overlap. It is therefore not necessary to apply the symmetrization postulate (*cf.* chap. XIV, §D-2-b).

b. CALCULATION OF THE ELECTROSTATIC INTERACTION ENERGY

Atom (A) creates at (B) an electrostatic potential U with which the charges of (B) interact. This gives rise to an interaction energy \mathcal{W} .

We saw in complement E_x that U can be calculated in terms of R , \mathbf{n} and the multipole moments of atom (A). Since (A) is neutral, the most important contribution to U is that of the electric dipole moment \mathcal{D}_A . Similarly, since (B) is neutral, the most important term in \mathcal{W} comes from the interaction between the dipole moment \mathcal{D}_B of (B) and the electric field $\mathbf{E} = -\nabla U$ which is essentially created by \mathcal{D}_A . This explains the name of "dipole-dipole interaction" given to the dominant term of \mathcal{W} . There exist, of course, smaller terms (dipole-quadrupole, quadrupole-quadrupole, etc.), and \mathcal{W} is written :

$$\mathcal{W} = \mathcal{W}_{dd} + \mathcal{W}_{dq} + \mathcal{W}_{qd} + \mathcal{W}_{qq} + \dots \quad (7)$$

To calculate \mathcal{W}_{dd} , we shall start with the expression for the electrostatic potential created by \mathcal{D}_A at (B) :

$$U(\mathbf{R}) = \frac{1}{4\pi\epsilon_0} \frac{\mathcal{D}_A \cdot \mathbf{R}}{R^3} \quad (8)$$

from which we see :

$$\mathbf{E} = -\nabla_{\mathbf{R}} U = -\frac{q}{4\pi\epsilon_0} \frac{1}{R^3} [\mathbf{r}_A - 3(\mathbf{r}_A \cdot \mathbf{n})\mathbf{n}] \quad (9)$$

and, consequently :

$$\mathcal{W}_{dd} = -\mathbf{E} \cdot \mathcal{D}_B = \frac{e^2}{R^3} [\mathbf{r}_A \cdot \mathbf{r}_B - 3(\mathbf{r}_A \cdot \mathbf{n})(\mathbf{r}_B \cdot \mathbf{n})] \quad (10)$$

We have set $e^2 = q^2/4\pi\epsilon_0$, and we have used expressions (4) and (5) for \mathcal{D}_A and \mathcal{D}_B . In this complement, we shall choose the Oz axis parallel to \mathbf{n} , so that (10) can be written :

$$\mathcal{W}_{dd} = \frac{e^2}{R^3} (x_A x_B + y_A y_B - 2z_A z_B) \quad (11)$$

In quantum mechanics, \mathcal{W}_{dd} becomes the operator W_{dd} , which can be obtained by replacing in (11) x_A, y_A, \dots, z_B by the corresponding observables X_A, Y_A, \dots, Z_B , which act in the state spaces \mathcal{E}_A and \mathcal{E}_B of the two hydrogen atoms^{*}:

$$W_{dd} = \frac{e^2}{R^3} (X_A X_B + Y_A Y_B - 2Z_A Z_B) \quad (12)$$

2. Van der Waals forces between two hydrogen atoms in the 1s ground state

a. EXISTENCE OF A $-C/R^6$ ATTRACTIVE POTENTIAL

α . Principle of the calculation

The Hamiltonian of the system is:

$$H = H_{0A} + H_{0B} + W_{dd} \quad (13)$$

where H_{0A} and H_{0B} are the energies of atoms (A) and (B) when they are isolated.

In the absence of W_{dd} , the eigenstates of H are given by the equation:

$$(H_{0A} + H_{0B}) | \varphi_{n,l,m}^A; \varphi_{n',l',m'}^B \rangle = (E_n + E_{n'}) | \varphi_{n,l,m}^A; \varphi_{n',l',m'}^B \rangle \quad (14)$$

where the $| \varphi_{n,l,m} \rangle$ and the E_n were calculated in §C of chapter VII. In particular, the ground state of $H_{0A} + H_{0B}$ is $| \varphi_{1,0,0}^A; \varphi_{1,0,0}^B \rangle$, of energy $-2E_I$. It is non-degenerate (we do not take spins into account).

The problem is to evaluate the shift in this ground state due to W_{dd} and, in particular, its R -dependence. This shift represents, so to speak, the interaction potential energy of the two atoms in the ground state.

Since W_{dd} is much smaller than H_{0A} and H_{0B} , we can calculate this effect by stationary perturbation theory.

β . First-order effect of the dipole-dipole interaction

Let us show that the first-order correction:

$$\varepsilon_1 = \langle \varphi_{1,0,0}^A; \varphi_{1,0,0}^B | W_{dd} | \varphi_{1,0,0}^A; \varphi_{1,0,0}^B \rangle \quad (15)$$

is zero. ε_1 involves, according to expression (12) for W_{dd} , products of the form $\langle \varphi_{1,0,0}^A | X_A | \varphi_{1,0,0}^A \rangle \langle \varphi_{1,0,0}^B | X_B | \varphi_{1,0,0}^B \rangle$ (and analogous quantities in which X_A is replaced by Y_A, Z_A and X_B by Y_B, Z_B), which are zero, since, in a stationary state of the atom, the mean values of the components of the position operator are zero.

* The translational external degrees of freedom of the two atoms are not quantized: for the sake of simplicity, we assume the two protons to be infinitely heavy and motionless. In (12), R is therefore a parameter and not an observable.

COMMENT:

The other terms, W_{dq} , W_{qd} , W_{qq} ..., of expansion (7) involve products of two multipole moments, one relative to (A) and the other one to (B), at least one of which is of order higher than 1. Their contributions are also zero to first order: they are expressed in terms of mean values in the ground state of multipole operators of order greater than or equal to one, and we know (cf. complement E_X, §2-c) that such mean values are zero in an $l = 0$ state (triangle rule of Clebsch-Gordan-coefficients). Therefore we must find the second-order effect of W_{dd} , which then constitutes the most important energy correction.

γ. Second-order effect of the dipole-dipole interaction

According to the results of chapter XI, the second-order energy correction can be written:

$$\varepsilon_2 = \sum_{\substack{n'l'm \\ n'l'm'}}' \frac{|\langle \varphi_{n,l,m}^A; \varphi_{n',l',m'}^B | W_{dd} | \varphi_{1,0,0}^A; \varphi_{1,0,0}^B \rangle|^2}{-2E_l - E_n - E_{n'}} \quad (16)$$

where the notation Σ' means that the state $|\varphi_{1,0,0}^A; \varphi_{1,0,0}^B\rangle$ is excluded from the summation*.

Since W_{dd} is proportional to $1/R^3$, ε_2 is proportional to $1/R^6$. Furthermore, all the energy denominators are negative, since we are starting from the ground state. Therefore, the dipole-dipole interaction gives rise to a negative energy proportional to $1/R^6$:

$$\varepsilon_2 = -\frac{C}{R^6} \quad (17)$$

Van der Waals forces are therefore attractive and vary with $1/R^7$.

Finally, let us calculate the expansion of the ground state to first order in W_{dd} . We find, according to formula (B-11) of chapter XI:

$$|\psi_0\rangle = |\varphi_{1,0,0}^A; \varphi_{1,0,0}^B\rangle + \sum_{\substack{n'l'm \\ n'l'm'}}' |\varphi_{n,l,m}^A; \varphi_{n',l',m'}^B\rangle \frac{\langle \varphi_{n,l,m}^A; \varphi_{n',l',m'}^B | W_{dd} | \varphi_{1,0,0}^A; \varphi_{1,0,0}^B \rangle}{-2E_l - E_n - E_{n'}} + \dots \quad (18)$$

COMMENT:

The matrix elements appearing in expressions (16) and (18) involve the quantities $\langle \varphi_{n,l,m}^A | X_A | \varphi_{1,0,0}^A \rangle$, $\langle \varphi_{n',l',m'}^B | X_B | \varphi_{1,0,0}^B \rangle$ (and analogous quantities in which X_A and

* This summation is performed not only over the bound states, but also over the continuous spectrum of $H_{0A} + H_{0B}$.



X_B are replaced by Y_A and Y_B or Z_A and Z_B), which are different from zero only if $l = 1$ and $l' = 1$. These quantities are indeed proportional to products of angular integrals

$$\left[\int Y_l^{m*}(\Omega_A) Y_1^q(\Omega_A) Y_0^0(\Omega_A) d\Omega_A \right] \times \left[\int Y_{l'}^{m'*}(\Omega_B) Y_1^q(\Omega_B) Y_0^0(\Omega_B) d\Omega_B \right]$$

which, according to the results of complement C_X, are zero if $l \neq 1$ or $l' \neq 1$. We can therefore, in (16) and (18), replace l and l' by 1.

b. APPROXIMATE CALCULATION OF THE CONSTANT C

According to (16) and (12), the constant C appearing in (17) is given by:

$$C = e^4 \sum_{\substack{n, l, m \\ n', l', m'}} \frac{|\langle \varphi_{n, l, m}^A; \varphi_{n', l', m'}^B | (X_A X_B + Y_A Y_B - 2Z_A Z_B) | \varphi_{1, 0, 0}^A; \varphi_{1, 0, 0}^B \rangle|^2}{2E_l + E_n + E_{n'}} \quad (19)$$

We must have $n \geq 2$ and $n' \geq 2$. For bound states, $|E_n| = E_l/n^2$ is smaller than E_l , and the error is not significant if we replace in (19) E_n and $E_{n'}$ by 0. For states in the continuous spectrum, E_n varies between 0 and $+\infty$. The matrix elements of the numerator become small, however, as soon as the size of E_n becomes appreciable, since the spatial oscillations of the wave function are then numerous in the region in which $\varphi_{1, 0, 0}(\mathbf{r})$ is non-zero.

To have an idea of the order of magnitude of C , we can therefore replace all the energy denominators of (19) by $2E_l$. Using the closure relation and the fact that the diagonal element of W_{dd} is zero (§2-a-β), we then get:

$$C \simeq \frac{e^4}{2E_l} \langle \varphi_{1, 0, 0}^A; \varphi_{1, 0, 0}^B | (X_A X_B + Y_A Y_B - 2Z_A Z_B)^2 | \varphi_{1, 0, 0}^A; \varphi_{1, 0, 0}^B \rangle \quad (20)$$

This expression is simple to calculate: because of the spherical symmetry of the $1s$ state, the mean values of the cross terms of the type $X_A Y_A$, $X_B Y_B$, ..., are zero. Furthermore, and for the same reason, the various quantities:

$$\langle \varphi_{1, 0, 0}^A | X_A^2 | \varphi_{1, 0, 0}^A \rangle, \langle \varphi_{1, 0, 0}^A | Y_A^2 | \varphi_{1, 0, 0}^A \rangle, \dots, \langle \varphi_{1, 0, 0}^B | Z_B^2 | \varphi_{1, 0, 0}^B \rangle$$

are all equal to one third of the mean value of $\mathbf{R}_A^2 = X_A^2 + Y_A^2 + Z_A^2$. We finally obtain, therefore, using the expression for the wave function $\varphi_{1, 0, 0}(\mathbf{r})$:

$$C \simeq \frac{e^4}{2E_l} \times 6 \left| \langle \varphi_{1, 0, 0}^A | \frac{\mathbf{R}_A^2}{3} | \varphi_{1, 0, 0}^A \rangle \right|^2 = 6 e^2 a_0^5 \quad (21)$$

(where a_0 is the Bohr radius) and, consequently:

$$\varepsilon_2 \simeq -6e^2 \frac{a_0^5}{R^6} = -6 \frac{e^2}{R} \left(\frac{a_0}{R} \right)^5 \quad (22)$$