Interaction between atoms and molecules

I. The long range van der Waals Interaction - Application of both perturbation and variational methods.

fig.

Consider two hydrogen atoms, A and B, separated by $\vec{R}$. We will calculate the interaction between the two atoms when the distance between them is large enough so that the electron clouds do not overlap, $R \gg a_0$. The interaction turns out to be attractive and is, for example, responsible for the condensation of rare gases into liquids and solids. It is present in the interaction of all atoms and molecules and is referred to as the *van der Waals* interaction or the *dispersion* interaction.

Consider two hydrogen atoms as an example. The discussion can easily be extended to larger atoms. An essential assumption here is that the distance between the atoms is large enough that the overlap of the electron wavefunctions can be neglected. Then there is no 'chemical' bond. At shorter, range where the overlap is significant, the problem is much harder and will be treated later (Hartree-Fock and beyond). For two hydrogen atoms with opposite spin, there will be an attractive bonding interaction which is much larger than the van der Waals interaction. But, for two hydrogen atoms with the same spin, the van der Waals interaction is the only attraction, the short range interaction is purely repulsive.

The Hamiltonian of the two atom system can be written as:

$$H = H_{0A} + H_{0B} + H'$$

where

$$H_{0A} \equiv -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{r_{1A}}$$

is the A atom Hamiltonian and

$$H_{0B} \equiv -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{r_{2B}}$$

is the B atom Hamiltonian, and the last part

$$H' \equiv \frac{e^2}{R} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{1B}}$$

is the one that gives rise to interaction between the two atoms. Note that the vectors $\vec{r}_1$ and $\vec{r}_2$ do not refer to the same origin.

We will first get an estimate of the interaction energy using perturbation expansion. It turns out that we can quite easily get a lower bound for the leading contribution to the van der Waals interaction in second order. Then variational calculations are used to obtain an upper bound. These kinds of calculations have been very successful in predicting the interaction of rare gas atoms and are currently being extended to more complicated systems.

Perturbation Calculation

The zeroth order Hamiltonian can be taken to be

$$H_0 = H_{0A} + H_{0B} \ .$$

Then the zeroth order eigenstates are product states since the $\vec{r}_A$ dependence separates from the $\vec{r}_B$ dependence. Each factor is simply a hydrogen atom wave function:

$$U(\vec{r}_A, \vec{r}_B) = U_{nlm}(\vec{r}_A)U_{n'\ell'm'}(\vec{r}_B) = < r_A|nlm >< r_B|n'\ell'm' > \ .$$

We assume the hydrogen atoms are in their ground state, $n = 1$, $\ell = 0$, $m = 0$, that is, the state vector for each atom is $|100 >$ and

$$U_0(\vec{r}_A, \vec{r}_B) = U_{100}(\vec{r}_A)U_{100}(\vec{r}_B) \ .$$

The function U_0 is an eigenfunction of H_0

$$H_0 U_0 = E_0 U_0$$

with eigenvalue

$$E_0 = -2E_I$$

where E_I is the ionization energy of a hydrogen atom. The last part of the Hamiltonian, H', which includes all the interactions between particles in different atoms, is treated as a perturbation. Since the distance between the atoms is assumed to be large, we can use an asymptotic form for the perturbation, obtained by expanding it in powers of $1/R$ (we take the molecular axis, $\vec{R}$, to be parallel to $\hat{z}$):

$$\frac{1}{r_{2A}} = \frac{1}{|\vec{R} + \vec{r}_2|} = \frac{1}{\sqrt{R^2 + r_2^2 + 2\vec{r}_2 \cdot \vec{R}}}$$

$$= \frac{1}{\sqrt{R^2 + r_2^2 + 2z_2 R}}$$

$$= \frac{1}{R} \frac{1}{\sqrt{1 + \frac{2z_2}{R} + (\frac{r_2}{R})^2}}$$

Similarly:

$$\frac{1}{r_{1B}} = \frac{1}{|\vec{r}_1 - \vec{R}|} = \frac{1}{R} \frac{1}{\sqrt{1 - \frac{2z_1}{R} + (\frac{r_1}{R})^2}}$$

and

$$\frac{1}{r_{12}} = \frac{1}{|\vec{r}_1 - (\vec{R} + \vec{r}_2)|} = \frac{1}{|(\vec{r}_1 - \vec{r}_2) - \vec{R}|}$$

$$= \frac{1}{|R + (\vec{r}_2 - \vec{r}_1)|} = \frac{1}{R} \frac{1}{\sqrt{1 + \frac{2(z_2 - z_1)}{R} + \frac{(\vec{r}_2 - \vec{r}_1)(\vec{r}_2 - \vec{r}_1)}{R^2}}} \quad .$$

Since $R >> a_0 \approx |r_1| \approx |r_2|$ we can Taylor expand:

$$\frac{1}{\sqrt{1 + \epsilon}} = 1 - \frac{\epsilon}{2} + \frac{3\epsilon^2}{8} \ (\text{h.o.t.})$$

Retaining all terms up to second order in the coordinates gives, for example,

$$\frac{1}{r_{2A}} \approx \frac{1}{R}\left(1 - \frac{z_2}{R} - \frac{1}{2}\left(\frac{r_2}{R}\right)^2 + \frac{3}{2}\left(\frac{z_2}{R}\right)^2\right).$$

Adding up the contributions from all terms in the perturbation gives

$$H' \approx \frac{e^2}{R^3}\left(x_1 x_2 + y_1 y_2 - 2 z_1 z_2\right)$$

to lowest order.

This expression could also be obtained by realizing that there is an instantaneous dipole moment at each atom

$$\vec{D}_A = e\vec{r}_1 \qquad \text{and} \qquad \vec{D}_B = e\vec{r}_2$$

The interaction energy between these two dipoles is the lowest order term in H'. The electrostatic potential at B created by the dipole $\vec{D}_A$ is

$$U(\vec{R}) = \frac{\vec{D}_A \cdot \vec{R}}{R^3} = \frac{e}{R^3}\ \vec{r}_1 \cdot \vec{R}$$

and the electric field is:

$$\vec{E}_{(R)} = -\nabla_R U = -\frac{1}{R^3}\left[\vec{r}_1 - 3(\vec{r}_1 \cdot \hat{R})\hat{R}\right]$$

The potential energy of dipole $\vec{D}_B$ in this field is:

$$-\vec{E} \cdot \vec{D}_B = \frac{e^2}{R^3}\left[\vec{r}_1 \cdot \vec{r}_2 - 3(\vec{r}_1 \cdot \hat{R})(\vec{r}_2 \cdot \hat{R})\right]$$

Taking this dipole-dipole interaction to be H' and using $\hat{R} = \hat{z}$ gives the same expression as obtained from the Taylor series expansions above. More systematically, we can expand H' in a multipole expansion, e.g.:

$$\frac{1}{|\vec{R} + \vec{r}_2|} = \frac{1}{R}\sum_{\ell=0}^{\infty}\left(\frac{e^2}{R^3}\right)^{\ell} P_{\ell}(\cos\alpha_2) = \quad \underset{\substack{\uparrow \\ \text{monopole}}}{\frac{1}{R}} \quad + \quad \underset{\substack{\uparrow \\ \text{dipole}}}{\frac{r_2 \cos\alpha_2}{R^2}} \quad + \quad \underset{\substack{\uparrow \\ \text{quadrupole, etc}}}{(\text{h.o.t.})}$$

$$= \frac{1}{R} + \frac{\vec{R} \cdot \vec{r}_2}{R^3} + (\text{h.o.t.})$$

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Then we see that the higher order terms in H' correspond to dipole-quadrupole, quadrupole-quadrupole, dipole-octupole, etc., interactions. We will only include the leading contribution, the dipole-dipole interaction, in H', i.e.

$$H'_{dd} = \frac{e^2}{R^3}\left(x_1 x_2 + y_1 y_2 - 2z_1 z_2\right)$$

First Order Perturbation:

$$\begin{aligned}
W_1 &= \frac{e^2}{R^3} < 100|x_1 x_2 + y_1 y_2 - 2z_1 z_2|100 > \\
&= \frac{e^2}{R^3}\int dr_1^3 \int d^3 r_2 U_{100}^2(r_1)U_{100}^2(r_2)\left(x_1 x_2 + y_1 y_2 - 2z_1 z_2\right) \\
&= 0
\end{aligned}$$

Since U_{100} is an even function but H'_{dd} is an odd function of each coordinate. (W_1 also vanishes for the higher order terms in H'.)

Second Order Perturbation:

$$W_2 = \sum_{n_A\neq 1}\sum_{\ell_A}\sum_{m_A}\sum_{n_B\neq 1}\sum_{\ell_B}\sum_{m_B}\frac{|<100|<100|H'_{dd}|n_A\ell_A m_A>|n_B\ell_B m_B>|^2}{E_0 - E_A - E_B} \quad .$$

We need to sum over all the excited states of atom A and B. Both $n_A = 0$ and $n_B = 0$ are excluded from the sum because those would give matrix elements that are zero, in analogy with the W_1 calculation. Since

$$E_0 = -2E_I \ < \ E_A + E_B$$

and the numerator of each term is necessarily positive, we must have $W_2 < 0$. That is, the energy difference between two interacting atoms, $E_0 + W_2$, and two isolated atoms, E_0, is negative, meaning the interaction is attractive. Also, each term in the sum varies as $1/R^6$. Therefore we know already that the van der Waals interaction looks like:

$$E_{dd} = W_2 = -\frac{C_6}{R^6}$$

where $C_6 > 0$ is a constant to be determined. The lowest energy state, included in the sum, has $n_A = n_B = 2$ and energy

$$E_* = E_A + E_B = -\frac{e^2}{2a_0}\left(\frac{1}{n_A^2} + \frac{1}{n_B^2}\right) = -\frac{e^2}{4a_0}$$

We can get a lower bound for W_2 by replacing $E_A + E_B$ for all the excited states in the formula by $-e^2/4a_0$, i.e.

$$W_2 \geq \frac{1}{E_0 - E_*}\sum_p |<0|H'|p>|^2$$

where p is a short hand for all the quantum numbers $(n_A, \ell_A, m_A, n_B, \ell_B, m_B)$ and $|0>$ is a short hand for $|100>$. Since $<0|H'|0>= 0$ (the ground state wave function is even but H' is odd) we can choose to include that term in the sum. We then have summation over a complete set of states

$$\sum_p |p><p| = 1$$

and

$$\sum_p |<0|H'|p>|^2 = \sum_p <0|H'|p><p|H'|0>=<0|H'^2|0>$$

so

$$W_2 \geq \frac{<0|H'^2|0>}{E_0 - E_*}$$

$$H'^2 = \frac{e^4}{R^6}\left(x_1 x_2 + y_1 y_2 - 2z_1 z_2\right)^2 = \frac{e^4}{R^6}\left(x_1^2 x_2^2 + y_1^2 y_2^2 + 4z_1^2 z_2^2 + \underbrace{2x_1 x_2 y_1 y_2}_{\text{gives zero}} + \ldots\right)$$

Only terms that are even in x, y, and z contribute to the matrix element $<0|H'^2|0>$. Evaluate the integrals:

$$\int x^2 U_{100}^2(r)d^3 r = \frac{1}{3}\int r^2 U_{100}^2(r)d^3 r$$

$$= \frac{1}{3\pi a_0^3}\int_0^\infty r^2 e^{-2r/a_0} 4\pi r^2 dr$$

$$= a_0^2 .$$

Therefore,

$$<0|H'^2|0>= 6\,\frac{e^4}{R^6}\,a_0^4$$

and

$$E_{dd}^{(2)} = W_2(R) \geq -\frac{8e^2 a_0^5}{R^6}.$$

This gives a lower bound on the dipole-dipole part of the van der Waals interaction. Written in terms of the C_6 coefficient, the result is

$$C_6 \geq 8e^2 a_0^5.$$

Variational calculation

    A variational calculation can be used to give an upper bound to the interaction energy. We know, from the perturbation calculation, that the interaction energy should go as $1/R^6$. We therefore choose trial functions that will generate such behavior. If we choose trial

functions, $\psi(\vec{r}_1, \vec{r}_2)$, that are independent of R, then the variational energy will go as $1/R^3$ rather than $1/R^6$. A convenient choice that generates the right R dependence is:

$$\psi_\alpha(r_1, r_2) = U_{100}(\vec{r}_1)U_{100}(\vec{r}_2)\big(1 + \alpha H'\big)$$

Here α is the variational parameter. The expectation value of the energy then becomes a function of this parameter:

$$W(\alpha) \equiv \frac{< \psi_\alpha|H_0 + H'|\psi_\alpha >}{< \psi_\alpha|\psi_\alpha >} \geq E_0 + E_{dd}$$

Recall that E_0 is the energy of two non-interacting hydrogen atoms in the ground state, $E_0 = -2E_I$. Let

$$U_0(\vec{r}_1, \vec{r}_2) \equiv U_{100}(\vec{r}_1)U_{100}(\vec{r}_2)$$

then

$$W(\alpha) = \frac{\int d^3r_1 \int d^3r_2 U_0(1 + \alpha H')(H_0 + H')U_0(1 + \alpha H')}{\int d^3r_1 \int d^3r_2 U_0^2(1 + \alpha H')^2}$$

the numerator becomes:

$$\int \int \bigg[\underbrace{U_0 H_0 U_0}_{E_0} + U_0 H' U_0 + \alpha U_0 H_0 U_0 H' + \alpha U_0 H' H_0 U_0 + 2\alpha U_0 H'^2 U_0$$

$$+ \alpha^2 U_0 H' H_0 H' U_0 + \alpha^2 U_0 H'^3 \bigg] d^3\vec{r}_1 d^3\vec{r}_2$$

Direct evaluation gives

$$\alpha^2 \int \int U_0 H' H_0 H' U_0 \ d\vec{r}_1 d\vec{r}_2 = 0 \ .$$

So, the numerator is

$$E_0 + 2\alpha < 0|H'^2|0 > \ .$$

The denominator is

$$\int \int d\vec{r}_1 d\vec{r}_2 \bigg[U_0^2 + U_0^2 2\alpha H' + U_0^2 \alpha^2 H'^2\bigg] = 1 + \alpha^2 < 0|H'^2|0 > \ .$$

Putting the two together gives

$$W(\alpha) = \frac{E_0 + 2\alpha < 0|H'^2|0 >}{1 + \alpha^2 < 0|H'^2|0 >} \ .$$

Taylor expanding the denominator gives

$$\simeq \Big(E_0 + 2\alpha < 0|H'^2|0 > \Big)\Big(1 - \alpha^2 < 0|H'^2|0 > + \text{(h.o.t.)}\Big)$$

$$= E_0 + \Big(2\alpha - E_0\alpha^2\Big) < 0|H'^2|0 > + \text{(h.o.t.)}$$

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Minimize with respect to α by setting the derivative to zero:

$$\frac{dW}{d\alpha} = (2 - 2E_0\alpha) < 0|H'^2|0 > = 0$$

$$\alpha_m = \frac{1}{E_0}.$$

The minimum energy is:

$$W(\alpha_m) = E_0 + E_{dd} = \frac{E_0 + \frac{2}{E_0} < 0|H'^2|0 >}{1 + \frac{1}{E_0^2} < 0|H'^2|0 >} \ .$$

The matrix element has already been given above in the perturbation calculation

$$< 0|H'^2|0 >= \frac{6e^4 a_0^4}{R^6}$$

and

$$E_0 = -2E_I = -\frac{e^2}{a_0}$$

which gives

$$W(\alpha_m) = E_0 - \frac{6e^2 a_0^5}{R^6} \geq E_0 + E_{dd} \ .$$

Therefore, an upper bound is obtained for the interaction energy:

$$E_{dd} \leq -\frac{6e^2 a_0^5}{R^6}.$$

Combining the two estimates, the lower bound obtained from perturbation theory and the upper bound obtained from variational calculations, we have:

$$-\frac{8e^2 a_0^5}{R^6} \leq E_{dd} \leq -\frac{6e^2 a_0^5}{R^6}.$$

A practical estimate can be obtained from the calculations by taking the average. The exact value must lie within this rather narrow range. More extensive calculations give

$$E_{dd} = -\frac{6.5e^2 a_0^5}{R^6} \ .$$