

VAN DER WAALS INTERACTION

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 6.31.

A simple one-dimensional model of the interaction between two electrically neutral hydrogen atoms can be constructed using the harmonic oscillator. Within each atom, we model the interaction between the proton and electron (in 1-d remember) as a spring with spring constant k :

$$(0.1) \quad H_i = \frac{p_i^2}{2m} + \frac{1}{2}kx_i^2; i = 1, 2$$

where x_i is the separation between the proton and electron in atom i .

The unperturbed energy (ignoring the interaction between the two atoms) of the system is then

$$(0.2) \quad H_0 = H_1 + H_2$$

$$(0.3) \quad = \frac{p_1^2}{2m} + \frac{1}{2}kx_1^2 + \frac{p_2^2}{2m} + \frac{1}{2}kx_2^2$$

Now if we add in the Coulomb interaction between the four particles (taking R to be the distance between the two protons, with atom 1 to the left of atom 2, and the proton to the left of the electron in each atom) we get the perturbation:

$$(0.4) \quad H' = \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{R} - \frac{1}{R-x_1} - \frac{1}{R+x_2} + \frac{1}{R-x_1+x_2} \right]$$

$$(0.5) \quad = \frac{e^2}{4\pi\epsilon_0 R} \left[1 - \frac{1}{1-x_1/R} - \frac{1}{1+x_2/R} - \frac{1}{1-(x_1-x_2)/R} \right]$$

where the first term is the interaction between the protons, the second is between proton 2 and electron 1, the third is between proton 1 and electron 2 and the last is between the two electrons. Note that the signs on the x s are opposite to that in Griffiths's equation 6.97 which is needed to match his figure 6.14; however, this doesn't affect the rest of the problem since only products of the x s occur.

If we assume that the spacing R between the atoms is much greater than the proton-electron spacing within each atom, we can expand H' in a Taylor series up to second order (the first order terms cancel) and get (e.g. using Maple's 'mtaylor' command, or by hand using $1/(1-x) = 1+x+x^2+\dots$) for the leading term:

$$(0.6) \quad H' = -\frac{e^2 x_1 x_2}{2\pi\epsilon_0 R^3} + \frac{1}{R} \mathcal{O}\left(\frac{x_i^3}{R^3}\right)$$

Thus perturbed hamiltonian is approximately

$$(0.7) \quad H_1 = \frac{p_1^2}{2m} + \frac{1}{2} k x_1^2 + \frac{p_2^2}{2m} + \frac{1}{2} k x_2^2 - \frac{e^2 x_1 x_2}{2\pi\epsilon_0 R^3}$$

We now make the change of variables:

$$(0.8) \quad x_{\pm} = \frac{1}{\sqrt{2}} (x_1 \pm x_2)$$

This has the inverse relation:

$$(0.9) \quad x_1 = \frac{1}{\sqrt{2}} (x_+ + x_-)$$

$$(0.10) \quad x_2 = \frac{1}{\sqrt{2}} (x_+ - x_-)$$

This results in a change in the momentum variables:

$$(0.11) \quad p_{\pm} = -i\hbar \frac{d}{dx_{\pm}}$$

$$(0.12) \quad = -i\hbar \left(\frac{\partial}{\partial x_1} \frac{\partial x_1}{\partial x_{\pm}} + \frac{\partial}{\partial x_2} \frac{\partial x_2}{\partial x_{\pm}} \right)$$

$$(0.13) \quad = -\frac{i\hbar}{\sqrt{2}} \left(\frac{\partial}{\partial x_1} \pm \frac{\partial}{\partial x_2} \right)$$

$$(0.14) \quad = \frac{1}{\sqrt{2}} (p_1 \pm p_2)$$

From here, it is straightforward (although tedious) algebra to substitute for $x_{1,2}$ and $p_{1,2}$ (e.g. using Maple's 'subs' command, followed by 'simplify' and 'expand') to get

$$(0.15) \quad H_1 = \frac{p_+^2}{2m} + \frac{1}{2} \left(k - \frac{e^2}{2\pi\epsilon_0 R^3} \right) x_+^2 + \frac{p_-^2}{2m} + \frac{1}{2} \left(k + \frac{e^2}{2\pi\epsilon_0 R^3} \right) x_-^2$$

The perturbed hamiltonian is thus the sum of two harmonic oscillators with spring constants

$$(0.16) \quad k_{\pm} = k \mp \frac{e^2}{2\pi\epsilon_0 R^3}$$

Note that Griffiths's equation 6.99 is wrong since the denominator in the second term should be $2\pi\epsilon_0 R^3$ as shown here, not $4\pi\epsilon_0 R^3$. This affects the rest of the question as well. Since the hamiltonian decouples into two independent oscillators, the ground state energy is

$$(0.17) \quad E = \frac{\hbar}{2}(\omega_+ + \omega_-)$$

$$(0.18) \quad \omega_{\pm} = \sqrt{\frac{k}{m} \mp \frac{e^2}{2\pi\epsilon_0 m R^3}}$$

We define the parameter

$$(0.19) \quad b \equiv \frac{e^2}{2\pi\epsilon_0 R^3}$$

Then the energy is

$$(0.20) \quad E = \frac{\hbar}{2\sqrt{m}} \left(\sqrt{k-b} + \sqrt{k+b} \right)$$

$$(0.21) \quad = \frac{\hbar}{2} \sqrt{\frac{k}{m}} \left(\sqrt{1-b/k} + \sqrt{1+b/k} \right)$$

Expanding this in a Taylor series in b/k we find that the first order term is zero so

$$(0.22) \quad E = \hbar \sqrt{\frac{k}{m}} \left(1 - \frac{1}{8} \frac{b^2}{k^2} + \dots \right)$$

$$(0.23) \quad = \hbar\omega_0 - \frac{\hbar}{8m^2\omega_0^3} \left(\frac{e^2}{2\pi\epsilon_0 R^3} \right)^2 + \dots$$

where $\omega_0 = \sqrt{k/m}$ is the unperturbed frequency of oscillation. This correction to the energy is responsible for the Van der Waals interaction between two neutral atoms.

We can do the same calculation using first and second order perturbation theory. The first order perturbation is

$$(0.24) \quad E_1 = \langle 00 | H' | 00 \rangle$$

where the state $|00\rangle$ is the unperturbed ground state for both oscillators. To work this out, we use the result for mean values of position that we derived earlier.

$$(0.25) \quad \langle n | x | n' \rangle = \sqrt{\frac{\hbar}{2m\omega}} \left(\sqrt{n'+1} \delta_{n,n'+1} + \sqrt{n'} \delta_{n,n'-1} \right)$$

We get

$$(0.26) \quad \langle 00 | H' | 00 \rangle = - \langle 00 | \frac{e^2 x_1 x_2}{2\pi\epsilon_0 R^3} | 00 \rangle$$

$$(0.27) \quad = - \frac{e^2}{2\pi\epsilon_0 R^3} \langle 00 | x_1 x_2 | 00 \rangle$$

$$(0.28) \quad = - \frac{e^2}{2\pi\epsilon_0 R^3} \langle 0 | x_1 | 0 \rangle \langle 0 | x_2 | 0 \rangle$$

We can split $\langle 00 | x_1 x_2 | 00 \rangle$ into $\langle 0 | x_1 | 0 \rangle \langle 0 | x_2 | 0 \rangle$ since x_1 and x_2 are independent coordinates so the average of one of them doesn't affect the other. From 0.25, both these averages are zero, so

$$(0.29) \quad E_1 = \langle 00 | H' | 00 \rangle = 0$$

and there is no first order correction to the energy, in agreement with the solution above.

For the second order correction we need $\langle n_1 n_2 | x_1 x_2 | 00 \rangle = \langle n_1 | x_1 | 0 \rangle \langle n_2 | x_2 | 0 \rangle$. Again, from 0.25, the only non-zero such matrix element is $\langle 1 | x | 0 \rangle = \sqrt{\frac{\hbar}{2m\omega_0}}$, so we get

$$(0.30) \quad E_2 = \left(- \frac{e^2}{2\pi\epsilon_0 R^3} \right)^2 \sum_{n_1, n_2 \neq 0} \frac{|\langle n_1 | x_1 | 0 \rangle \langle n_2 | x_2 | 0 \rangle|^2}{\hbar\omega_0 - E_{n_1 n_2, 0}}$$

$$(0.31) \quad = \left(\frac{e^2}{2\pi\epsilon_0 R^3} \right)^2 \left(\frac{\hbar}{2m\omega_0} \right)^2 \frac{1}{\hbar\omega_0 - E_{11,0}}$$

The unperturbed energy $E_{11,0}$ is

$$(0.32) \quad E_{11,0} = \frac{3}{2}\hbar\omega_0 + \frac{3}{2}\hbar\omega_0 = 3\hbar\omega_0$$

so the second order perturbation is

$$(0.33) \quad E_2 = \left(\frac{e^2}{2\pi\epsilon_0 R^3}\right)^2 \left(\frac{\hbar}{2m\omega_0}\right)^2 \left(-\frac{1}{2\hbar\omega_0}\right)$$

$$(0.34) \quad = -\frac{\hbar}{8m^2\omega_0^3} \left(\frac{e^2}{2\pi\epsilon_0 R^3}\right)^2$$

which agrees with the earlier result.