Van der Waals forces between Hydrogen atoms

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Abstract: Interactions between hydrogen atoms separated by a distance much larger than their radius will be studied in this essay. It will be done by calculating the energy of an isolated system in which there are only two atoms. In order to find the non-trivial result perturbation theory will be used and we will deduce the interaction by interpreting the resulting energy. Afterwards, another scenario with a first excited hydrogen atom and a ground one will be studied and we will compare both results. Since the $2p$ orbital does not have spherical symmetry, a stronger interaction will be found. Finally we will cover some particles which may have similar interactions when put in the same scenario and, lastly we will study the results collected through the paper.

I. INTRODUCTION

A hydrogen atom is a charge neutral particle which contains a single proton and an electron bound by the Coulomb force. When it is at ground state, its electronic configuration is $1s^1$. The s orbit in which the electron locates has spherical symmetry and, therefore, its probability distribution has no angular dependence.

Given this information, it would make sense to assume interactions between two far away hydrogen atoms to be non existent. Although the logical approach of this assumption, reality states the opposite. A Van der Waals force arises between them.
In this project we will study this interaction from a quantum approach. First, we will describe the interaction between two hydrogen atoms in ground state. Afterwards, we will describe the interaction of an atom in ground state and another in the first excited state $n = 2$. Then, we will consider other particles which could interact similarly in certain scenarios and describe the main differences we encounter in them. And lastly, we will finish with the conclusions and an analysis of the results.

II. 1S-1S HYDROGEN ATOM INTERACTION

In order to start this project, we will theoretically deduce the effective interaction of two hydrogen atoms with their electrons in the ground state $1s$. We start with a system made up by these two atoms at a distance much larger than Bohr's radius (a_o), which reflects the atom's size: $R >> a_o$. The system is summarized in FIG. 1:

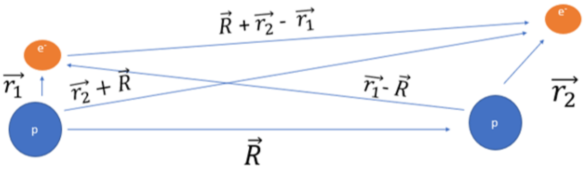

FIG. 1: Electrons (red) and protons (blue) and their relative positions

A. Perturbation theory

Proton-electron interactions from each atom are far stronger than the ones between both atoms. In order to find the potential between them, we will see the hydrogen-hydrogen interaction as a perturbation of each hydrogen eigenstate. The hamiltonian of the system is:

$$H = H_o + H' \quad (1)$$

$$H_o = -\frac{\hbar^2}{2\mu}(\Delta_1 + \Delta_2) - \frac{e^2}{r_1} - \frac{e^2}{r_2} \quad (2)$$

$$H' = -\frac{e^2}{R} + \frac{e^2}{|\vec{R} + \vec{r_2} - \vec{r_1}|} - \frac{e^2}{|\vec{R} + \vec{r_2}|} - \frac{e^2}{|\vec{R} - \vec{r_1}|} \quad (3)$$

Where H_o corresponds to the two isolated atoms and H' as the perturbation. The wave function of each hydrogen atom is:

$$\psi_{1,0,0} = (\frac{1}{a_o})^{3/2}\sqrt{\frac{1}{\pi}}e^{-\frac{r}{a_o}} \quad (4)$$

The wave function has spherical symmetry. We combine both unperturbed waves and obtain:

$$\psi_0^{(0)} = (\frac{1}{a_o})^3\frac{1}{\pi}e^{-\frac{r_1+r_2}{a_o}} \quad (5)$$

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In addition, the energy of each atom is:

$$E_n = -\frac{\mu(\alpha c)^2}{2n^2} \tag{6}$$

Where α is the fine structure constant and μ the reduced mass of the hydrogen atom. For two ground state hydrogen atoms, the system's energy is, therefore:

$$E_T = -\mu(\alpha c)^2 \tag{7}$$

It is important to keep in mind that, since the nucleus mass is much larger than the electron one, we consider protons to be frozen in space while electrons arrange themselves. This is known as Born-Oppenheimer approximation and enables us to use these eigenstates.
Now, we will expand the perturbation Hamiltonian in powers of r_i/R, since we assume that the distance between atoms is far larger than the average proton-electron atomic distance a_o ($R >> a_o$). By taking the expansion to the third power of $1/R$ we end up with the perturbation Hamiltonian:

$$H' = e^2(\frac{\vec{r_1}\cdot\vec{r_2}}{R^3} - 3\frac{(\vec{r_1}\cdot\vec{R})(\vec{r_2}\cdot\vec{R})}{R^5}) \tag{8}$$

We start with the first order perturbation:

$$E_n^{(1)} = <\psi_n^{(0)}|H'|\psi_n^{(0)}> \tag{9}$$

By parity, for $n = 1$:

$$E_1^{(1)} = 0 \tag{10}$$

We now proceed to calculate the second order of perturbations. In order to do so, we use:

$$E_0^{(2)} = \sum_{m\neq 0} \frac{|<\psi_0^{(0)}|H'|\psi_m^{(0)}>|^2}{E_m^{(0)} - E_0^{(0)}} \tag{11}$$

We manipulate the equation so it looks similar to the zeroth order one in equation (7):

$$E_0^{(2)} = -\mu(\alpha c)^2(\frac{a_o}{R})^6\zeta \tag{12}$$

$$\zeta = \frac{\hbar^2}{\mu a_0^6} \sum_{m\neq 0} \frac{|<\psi_0^{(0)}|S|\psi_m^{(0)}>|^2}{E_m^{(0)} - E_0^{(0)}} \tag{13}$$

$$S = \vec{r_1}\cdot\vec{r_2} - 3(\vec{r_1}\cdot\hat{R})(\vec{r_2}\cdot\hat{R}) \tag{14}$$

Finding ζ is complex since it requires the summation of the S operator over an infinite number of states with the ground one. Since we can not sum the series analytically, we find a bound. Notice that an upper bound is found by replacing in (13) all the excited energies by E_1, which by equation (6) is:

$$E_1 = -\frac{\mu(\alpha c)^2}{4} \tag{15}$$

Therefore, other terms of the summation will have a denominator larger than $3\frac{\mu(\alpha c)^2}{4}$. Hence:

$$\zeta \leq \frac{4}{3a_o^4} \sum_{j\neq 0} |<\psi_0^{(0)}|S|\psi_j^{(0)}>|^2 \tag{16}$$

Using the closure relation property, knowing that $<\psi_o^{(0)}|S|\psi_o^{(0)}> = 0$ and taking advantage of the spherical symmetry:

$$\int d^3x f(\vec{x}) x_i x_j = \frac{\delta_{ij}}{3}\int d^3x f(\vec{x})\vec{x}^2 \tag{17}$$

We finally obtain the upper bound for ζ in (13), which means a lower bound for the total second order perturbation energy:

$$\zeta \leq \frac{8}{9a_o^4} <\psi_0^{(0)}|\vec{r_1}\cdot\vec{r_2}|\psi_1^{(0)}> \approx 8 \tag{18}$$

$$E_o < -\mu(\alpha c)^2[1 + 8(\frac{a_o}{R})^6] \tag{19}$$

The final result of the perturbative calculation shows us that the dependence of the interaction upon the distance R is proportional to $1/R^6$.

B. Variational method

In order to find the upper bound we use the variational method. We use the following *ansatz*:

$$\psi(\vec{r_1},\vec{r_2}) = (\frac{1}{a_o})^3\frac{1}{\pi}e^{-\frac{r_1+r_2}{a_o}}[1 + AH'] = \psi_0^{(0)}[1 + AH'] \tag{20}$$

Where A [1] is the parameter to be optimized and H' the perturbative term introduced in equation (8). Now, we proceed to find the average energy as well as the value of A:

$$\begin{aligned} <H>_\psi = & \frac{<\psi|H_o + H'|\psi>}{<\psi|\psi>} \\ = & \frac{<0|(1 + AH')(H_o + H')(1 + AH')|0>}{<0|(1 + AH'+)^2|0>} \end{aligned} \tag{21}$$

(In order to facilitate the mathematical understanding of the procedure I have labelled $|0>$ to the system's ground wave function.)

$$<H>_\psi = \frac{E_o + <0|H'H'|0> + A^2 <0|H'H_oH'|0>}{1 + A^2 <0|H'H'|0>} \tag{22}$$

We first localize the unperturbed energy, then we calculate the squared perturbed Hamiltonian.

$$H'H' = \frac{e^4}{R^6}((\vec{r_1}\cdot\vec{r_2})^2 + 9(\vec{r_1}\cdot\hat{R})^2(\vec{r_2}\cdot\hat{R})^2 - 6(\vec{r_1}\cdot\vec{r_2})(\vec{r_1}\cdot\hat{R})(\vec{r_2}\cdot\hat{R})) \tag{23}$$

Both first terms cancel themselves because of spherical symmetry. We calculate the last term and obtain:

$$< 0|H'H'|0 >= \frac{6(ea_o)^4}{R^6} \tag{24}$$

We solve the last term from equation (22) by using commutation properties between H' and H_0:

$$\begin{aligned} &< 0|H'[H_o, H']|0 > + < 0|H'H'H_o|0 >= \\ &\qquad < 0|H'[H_o, H']|0 > +E_o < 0|H'H'|0 > \end{aligned} \tag{25}$$

The term $< 0|H'H'|0 >$ has been calculated in equations (24) and (7). We operate the commutation between H_1 and H_0 knowing that it results in the operator $\frac{1}{r_1}\frac{\partial}{\partial r_1}$:

$$< 0|H_1[H_o, H_1]|0 >= \frac{\hbar^2}{\mu} < 0|H_1H_1\frac{1}{r_1}\frac{\partial}{\partial r_1}|0 > \tag{26}$$

Finally, applying the spherical property of equation (17):

$$< 0|H_1[H_o, H_1]|0 >= \frac{6\mu(\alpha c)^2(ea_o)^4}{R^6} \tag{27}$$

Now that we know all the terms, equation (22) reads:

$$< H >_\psi = \frac{-\mu(\alpha c)^2 + A\frac{12(ea_o)^4}{R^6}}{1 + A^2\frac{6(ea_o)^4}{R^6}} \tag{28}$$

Given that a_o is much smaller than R we apply first order Taylor expansion and omit terms with denominators with R of power smaller than -6.

$$< H >_\psi \simeq -\mu(\alpha c)^2 + \frac{6(ea_o)^4}{R^6}[2A + \mu(\alpha c)^2A^2] \tag{29}$$

When minimizing $< H >_\psi$, we obtain that the value of our variational parameter is $A = -1/\mu(\alpha c)^2$. When applying it to the energy equation (30) we get:

$$E_{var}(R) = -\mu(\alpha c)^2[1 + 6(\frac{a_o}{R})^6] < E(R) \tag{30}$$

This conclusion shows us a lower bound of ζ. After our two theoretical approaches we conclude that:

$$6 \leq \zeta \leq 8 \tag{31}$$

The empirical result is $\zeta = 6.5$ [1], which is compatible with equation (31).

III. 1S-2P HYDROGEN ATOM INTERACTION

If in the same two hydrogen system, one of them is at an energy level $n = 2$, the system becomes eightfold degenerate:$|\psi^a_{1,0,0};\psi^b_{2,0,0} >; |\psi^a_{2,0,0};\psi^b_{1,0,0} >; |\psi^a_{1,0,0};\psi^b_{2,1,m} >; |\psi^a_{2,1,m'};\psi^b_{1,0,0} >$ where m,m'=-1,0,1. Notice that we now label the two atoms a and b, this is to simplify the reading. In addition, we put the two atoms in the z axis: $\vec{R} = R\hat{z}$. In order to solve the elements of the $8x8$ matrix we check the possible quantum state interactions with our perturbed Hamiltonian, that way we will find the first order perturbation energy.

$$H' = \frac{e^2}{R^3}(\vec{r_a}\cdot\vec{r_b} - 3(\vec{r_a}\cdot\hat{z})(\vec{r_b}\cdot\hat{z})) = \frac{e^2}{R^3}(x_ax_b + y_ay_b - 2z_az_b) \tag{32}$$

Now, we can manipulate it and obtain an easy to integrate spherical harmonic $(Y_{l,m})$ expression:

$$H' = \frac{e^2}{R^3}\frac{4\pi r_ar_b}{3}[Y^a_{1,-1}Y^b_{1,-1}{}^* + Y^a_{1,1}Y^b_{1,1}{}^* - 2Y^a_{1,0}Y^b_{1,0}{}^*] \tag{33}$$

We can now decompose the $8x8$ interaction matrix into four $2x2$ matrices. As we saw in equation (10), first order perturbation energy from two s orbital atoms is null, the others have the form:

$$\begin{pmatrix} 0 & k_m \\ k_m & 0 \end{pmatrix} \tag{34}$$

Where k_m will depend on the privileged direction of the p orbital and can be easily calculated by using the spherical harmonics of each hydrogen atom. We proceed to calculate k_m for all three possibilities. Since we are using spherical harmonics we start solving the rigid angle integral:

$m = 0$

$$\int d\Omega_b \int d\Omega_a Y^a_{1,0}{}^* Y^b_{0,0}{}^*(\frac{4\pi r_ar_b}{3}[-2Y^a_{1,0}Y^b_{1,0}{}^*])Y^a_{0,0}Y^b_{1,0} = -\frac{2r_ar_b}{3} \tag{35}$$

$m = -1$

$$\int d\Omega_b \int d\Omega_a Y^a_{1,0}{}^* Y^b_{0,0}{}^*(\frac{4\pi r_ar_b}{3}[Y^a_{1,-1}Y^b_{1,-1}{}^*])Y^a_{0,0}Y^b_{1,0} = \frac{r_ar_b}{3} \tag{36}$$

$m = 1$

$$\int d\Omega_b \int d\Omega_a Y^a_{1,0}{}^* Y^b_{0,0}{}^*(\frac{4\pi r_ar_b}{3}[Y^a_{1,1}Y^b_{1,1}{}^*])Y^a_{0,0}Y^b_{1,0} = \frac{r_ar_b}{3} \tag{37}$$

Since the radial integral is the same for both electrons, we calculate it once and square it:

$$\begin{aligned} &\int_0^\infty dr_ar_a^2R^*_{1,0}R_{2,1}r_a \int_0^\infty dr_br_b^2R^*_{1,0}R_{2,1}r_b = \\ &\qquad = [\int_0^\infty drr^2R^*_{1,0}R_{2,1}r]^2 = a_o\frac{2^{15}}{3^9} \end{aligned} \tag{38}$$

Now that we know both integrals, we reveal the values of k_m:

$$k_{1,-1} = \frac{e^2}{R^3}\frac{a_o^2 2^{15}}{3^{10}} = \frac{k_0}{2} \tag{39}$$

We diagonalize the matrices and find the following eigenvalues:

$$\lambda = \pm k_m \tag{40}$$

These results bring us very remarkable information. $m = 1, -1$ interaction is half the value of that of $m = 0$. For $1s$, $2p$ hydrogen atoms, there are four possible interactions:

$$m = 1, -1 \quad W = \pm\frac{e^2}{R^3}\frac{a_o^2 2^{15}}{3^{10}} \tag{41}$$

$$m = 0 \quad W = \pm\frac{e^2}{R^3}\frac{a_o^2 2^{16}}{3^{10}} \tag{42}$$

Furthermore, it is worth highlighting that in this system we have not had the need of applying second order perturbation theory in order to find the interactions because the system does not fulfill as many symmetries as the first one.
If we wanted to find the interaction between $1s$ and $2s$ hydrogen atoms we would have to go to second order perturbation theory as we did in the $1s$, $1s$ case.

IV. OTHER PARTICLES WITH SIMILAR INTERACTIONS

As we have proceeded with the study of this interaction we have only talked about hydrogen atoms. But it seems logical to apply it to other atoms or particles with similar properties. In this section I will explain some similar cases and make clear why they can not follow the exact same approach we have given to our hydrogen case.

A. Hydrogenoid atoms

Hydrogenoid atoms are any atom which possesses a single electron. Since the nucleus mass is much larger than that of the electron, it makes the reduced mass more similar to m_e .
But we encounter a different problem. $1 < Z$ hydrogenoid atoms are positive ions by definition, so that greatly disturbs our initial system. Since there appears a much stronger electromagnetic interaction between both atoms it would overshadow the one we are looking for in this project.
Even though, the perturbation we study would essentially remain the same, the energy of the system would add an extra energy related to the repulsive electromagnetic interaction between both ions.

B. Positronium

Positronium is a system consisting of an electron and a positron. Considering the short lifetime of them, it would be hard to prove this interaction. But theoretically we can consider the physical outcome of it.
The biggest problem with positronium is that the mass of the positron and the electron is the same and so we can not apply the Born-Oppenheimer approximation on it. Born-Oppenheimer approximation assumes that electrons are much faster than nuclei because of the difference of masses. Therefore, we can assume the nucleus to be frozen in a certain state and the electrons to arrange themselves consequentially. In both mathematical procedures, we have started assuming the frozen position of both nuclei at a distance $\vec{R}$ and then we have calculated the interactions by operating with both electron distances from their nucleus.
In positronium, the distance $\vec{R}$ would be as much of a variable as $\vec{r_1}$ or $\vec{r_2}$. Keeping it constant would differ so much the physical problem from ours that the final result would be physically meaningless.

C. Muonic atom

In a muonic hydrogenoid atom, a muon orbits the nucleus. Due to its high resting mass the average radial distance between the muon and the nucleus is very small. So much, that the quark distribution becomes relevant. That makes the muon more susceptible to angular differences in the potential field, since it stops being central. This creates a privileged angular position and disturbing the spherical symmetry of the s orbital. Since the atom tends to a polarity, the interaction hamiltonian drastically changes.
The shift on the perturbation hamiltonian completely denies the procedure since H' in equation (8) can no longer be applied.
Also, since muonium has a larger mass than electrons, Born-Oppenheimer approximation is not as useful, and limits the coherence of the atomic approach.

D. Hadronic atom

Hadronic atoms consist of an atomic nucleus (we will consider a single proton) and a negatively charged hadron. An example of hadronic components of this exotic atom are charged pions.
As with muons in muonic atoms, hadrons also tend to get

close to the nucleus and alter Born-Oppenheimer approximation, which disturbs our calculations with their lack of spherical symmetry. But, in addition, the alteration is even larger since they can interact via strong force with nucleons.
Strong force bonds need a short distance in order to be significant, but once hadrons are close enough, the interaction is far greater than the electromagnetic one. Therefore, if the hadron is located in a low energy electronic orbital, it will probably interact with the proton's quarks and quantum chromodynamics will step in our initial Hamiltonian. That would make the hadron to tend to a location where it minimizes the strong force and polarize the atom, altering the final $1/R$ dependence.

V. CONCLUSION

We have studied the interaction between two hydrogen atoms separated at a great distance in two different scenarios.
Firstly, having them both at ground level, the spherical symmetry of both atoms has been reflected on the first order perturbation, where we have seen a lack of interaction. Due to the impossibility of calculating the second order summation, we have found an upper bound with dependence R^{-6}. Later on, we have found the lower bound also with a R^{-6} dependence, by using the variational method with a wave function given in [1]. The physical interpretation of it is that both hydrogen atoms at $1s$ state have instantaneous polarizations where they induce one another a very weak electric field which makes them tend to lower the system energy by getting closer until a repulsive force given by electromagnetic force balances it out. The outcome would be similar to that of Lennard-Jones, which describes Van der Waals attraction force with R^{-6} at large distances.

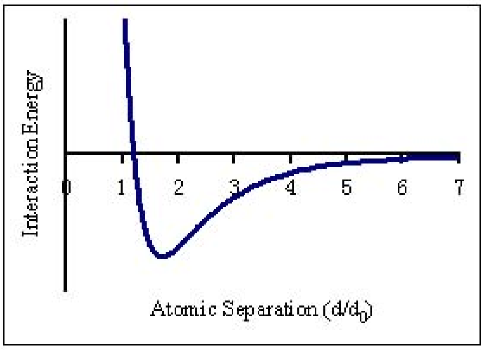

FIG. 2: Lennard-Jones potential

In addition, we consider the significance of the field delay. If the distance between both hydrogen atoms is much larger than the wavelengths (λ_o) from electronic state transitions then the dependence becomes R^{-7} [4].
Afterwards, we have successfully calculated the interaction between two hydrogen atoms at ground and first excited levels respectively. The results have been significantly different than the earlier ones. Due to the angular dependence of the excited hydrogen atom, the interaction is much stronger and has a dependence $1/R^3$. Not only that, but there are four possible eigenvalues depending on the magnetic quantum number (m_l) for the orbital $p(l = 1)$. While $m_l = 1, -1$ are degenerate, they describe orthogonal orbitals to the direction $\vec{R}$. Them and $m_l = 0$ have an attractive and a repulsive eigenvalue, meaning that the character of the interaction ultimately depends on the angular momentum eigenstate of the system.
By the end, we covered some particles which could seem valid to interact similarly and have observed why their physical properties invalidate this mathematical approach.
In conclusion, this procedure is physically consistent but it is important to see the mathematical assumptions it implies. We have expanded the perturbed hamiltonian as a series to the power of $(\frac{a_o}{R})^3$, so we start having an implicit correction of order O(3). Moreover, perturbation theory also consists of approximation in a double expansion approximation in inverse powers of R, and in α . Here we retained the leading contribution which is, by far, the most significant, $(\frac{a_o}{R})^6$ and α^2, which is of order $10^{-5} \cdot 1$. From a physics context it is a good approximation if corrections from both perturbation theory and the Taylor expansion are so small that neglecting them does not bring a meaningful change to our results. That is, while R covers ranges of $a_o << R << \lambda_o$, our results are excellent.
Van der Waals forces between neutral bodies are a purely quantum effect, which can not be determined via newtonian physics and which shows the power of quantum mechanics in atomic scale phenomena.
Finally, I would like to thank professor Josep Taron for his assistance through the course of his essay. His help has contributed greatly to my understanding of the topic and the way to express it in the essay.

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