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## Van der Waals interaction of ground state energy on ion molecular Hydrogen $H_2^+$

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**Abstract.** Hydrogen molecular ions are formed from Hydrogen molecules ( $H_2$ ) that lose one electron due to a particular process, such as ionization.  $H_2^+$  is a ionic molecule and one of the interstellar molecules. When  $H_2^+$  vibrates, inter-core interactions will occur. The interaction takes place from between the point dipole and the farthest proton. These interactions are called Van der Waals interactions. Van der Waals interaction is one of the interactions that occur in  $H_2^+$ , in addition to ionisation energy. The presence of van der Waals interactions on  $H_2^+$  will produce a certain energy whose value is small. In previous research, it has been shown that Van der Waals interaction will decrease the energy value of solid and liquid structures. In this research, we calculate energy on ion molecular hidrogen  $H_2^+$  as a second order perturbation theory. Using data from Herzberg, the  $n = 0$  vibrational energy level with harmonic oscillator approximation was obtained corresponding to Born-Oppenheimer potential. Based on perturbation theory, the vibrational energy varies with the order of  $R^{-4}$ . The simulations of vibrational wave functions both unperturbed and perturbed by van der Waals interaction show that difference between them is not significant. In particular, it is shown that the van der Waals interaction influence the shifting of the equilibrium point of  $H_2^+$  which depends on the parameter and internuclear separation. Ground state energy on ion molecular Hidrogen  $H_2^+$  in van der walls interaction is 0.087664 eV to 0.140693 eV.

### 1. Introduction

Harmonic oscillators can be solved entirely in both classical and quantum mechanics. In classical mechanics, the equation used is the second law of Newton about motion. While in quantum mechanics the equation used is second order differential equation found by Erwin Schrodinger and better known as the Schrodinger equation. Schrodinger equation can provide information about the nature of particles and waves on the system simultaneously. This is because the world of petals applies the dualism of particle waves. Schrodinger equation in the direction of 1 dimension consists of kinetic energy and potential work [1]. The harmonic oscillator has the lowest energy level known as zero-point energy. This condition results in stability in the atom so that the electrons will not fall into the nucleus [2]. One of the applications of harmonic oscillators in the quantum world is the phenomenon of diatomic molecular vibrations. The vibrational energy of the molecules can be solved with quantum oscillators [3].

A molecule is a group of neutral atoms bonded together so strongly that it behaves like a single particle. The molecule can absorb and emit electromagnetic radiation by altering the state of its



vibrational motion. A molecule that absorbs electromagnetic radiation will occupy an excitation state, then it will return to its ground state by emitting electromagnetic radiation. Molecular vibration motion depends on the interaction between protons, whereas the effect of the electron is ignored because its mass is too small when compared to the mass of the proton. The simplest form of vibration is a diatomic atom which has only a vibration mode. One example is the Hydrogen ion-molecule ( $H_2^+$ ).

Hydrogen molecular ions are formed from Hydrogen molecules ( $H_2$ ), indicating that it loses one electron due to a particular process such as ionization.  $H_2^+$  is a nonpolar molecule and one of the interstellar molecules. When  $H_2^+$  vibrates, inter-core interactions will occur. The interaction takes place from between the point dipole and the farthest proton. These interactions are called Van der Waals interactions [4]. This interaction is a weak attraction that occurs due to the electrical properties of a molecule. Van der Waals interaction is one of the interactions that occur in  $H_2^+$ , in addition to ionisation energy. The presence of van der Waals interactions on  $H_2^+$  will produce a certain energy whose value is small. In previous research, it has been shown that Van der Waals interaction will decrease the energy value of solid and liquid structures [5]. As a result, Hamiltonian system becomes changed and become complex, so to solve it required an approach method that is interference theory. In this study, the order level used is to the second order. The theory of interference is very good for determining discrete energy value changes and system eigen function due to small disturbances, provided that the functionality and eigenvalues of the system are known. This research will analyse the effect of van der Waals interaction on hydrogen molecular ion harmonic oscillator ( $H_2^+$ ) by using the theoretical approach method. This disorder will affect the energy of connective, dissociation energy and basic energy. The binding energy, the dissociation energy, and the total energy of ion Hydrogen molecular increase as the magnetic field strength increases [6].

## 2. Methods

### Motion Vibration for $H_2^+$

The interaction between protons and protons in the molecule  $H_2^+$  will result in molecular vibrations [7]. The motion equation used to describe the vibrational motion of  $H_2^+$  is by using the Schrodinger equation. By defining  $\psi_N$  as a wave function of  $H_2^+$  and  $U(r)$  is a certain potential energy acting on the system. The Hamiltonian equation can be written as,

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 + U(r)\right)\psi_N(r) = E\psi_N(r) \quad (1)$$

Laplacian operator ( $\nabla^2$ ) used in this research spherical coordinate. While  $\mu$  is reduction mass from two atoms, in Mathematics it can be expressed with,

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \quad (2)$$

The wavefunction in equation (1) is split into two parts namely the radial and the angular portions [8]. Radial wavelength function will cause vibration motion while angular wave function causes rotation motion. Because this study deals with the motion of vibration only, then the quantum number of azimuth used is zero ( $l = 0$ ). The wave function separation is shown in equation (3).

$$\psi_N = \chi(R)Y_{rot}(\theta, \phi) \quad (3)$$

The potential energy working at the molecular nucleus around the equilibrium point of  $r_e$  in quantum mechanics is,

$$U(x) = \frac{1}{2}m\omega^2x^2 \quad (4)$$

Thus, the Schrodinger equation in (1) becomes,

$$\left(\frac{\hbar}{2\mu}\frac{\partial^2\psi_{vib}}{\partial x^2} + \frac{1}{2}m\omega^2x^2\psi_{vib}\right) = E_{vib}\psi_{vib} \quad (5)$$

This equation describes the vibrational motion of hydrogen molecular ions with the harmonic potential of a one-dimensional oscillator. In this research, vibration motion on the ground state. In quantum mechanics will be observed. Harmonic oscillators have quantization energies of,

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \quad (6)$$

With wave function is,

$$\psi_n = A_n(a_+)^n e^{-\frac{m\omega x^2}{2\hbar}} \quad (7)$$

Where  $a_+$  is the raising operator with the form of the equation:

$$a_+ = \frac{1}{\sqrt{2m}} \left( \hbar \frac{d}{dx} + im\omega x \right) \quad (8)$$

### 3. Interaction Van der Waals

The hydrogen molecule ion has two states, symmetry and anti-symmetric state. The state of symmetry is a condition that allows the occurrence of molecular bonds where the probability of finding the largest electron is between the two protons. The electric field generated by protons polarizes the Hydrogen atom into an induced dipole. The interaction between protons and induced dipoles results in Van der Waals forces. The van der Waals forces in hydrogen molecular ions which produce a potential can be expressed by,

$$W = \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r} - \frac{1}{r-x} \right) \approx -\frac{e^2 x}{4\pi\epsilon_0 r^2} \quad (9)$$

With  $x$  is the distance between the electron and the proton in the Hydrogen atom, whereas  $r$  is the distance between the protons. Van der Waals styles can occur if  $r \gg x$ .

### 4. Time-Independent Perturbation Theory for Non-Degenerate System

In this study, the approach used is the theory of time-independent disorder. The usual disorder theory is also called Rayleigh-Schrodinger Perturbation Theory [9]. A Hamiltonian initial condition without any perturbation is shown in equation (10),

$$H\psi_n = E_n^{(0)}\psi_n \quad (10)$$

In perturbation Theory, The Hamiltonian System is broken down into two main parts, the unperturbed Hamiltonian ( $H_0$ ) and disturbed Hamiltonian ( $W$ ). In equation (11),  $\alpha$  means the expansion parameter for the perturbation correction order [10]. The hamiltonian system can be written as.

$$H = H_0 + \alpha W \quad (11)$$

Because the perturbation  $W$  assumed to be small, it should be possible to expand  $\psi_n$  and  $E_n$  as a power series in  $W$ . The expansion of energy and wave function are,

$$E = E^{(0)} + \alpha E^{(1)} + \alpha^2 E^{(2)} + \dots \quad (12)$$

$$\psi = \psi^{(0)} + \alpha \psi^{(1)} + \alpha^2 \psi^{(2)} + \dots \quad (13)$$

And then eq. (6), eq. (12) and eq. (13) is substituted to eq. (10).

$$(H_0 + \alpha W)(\psi^{(0)} + \alpha \psi^{(1)} + \alpha^2 \psi^{(2)} + \dots) = (E^{(0)} + \alpha E^{(1)} + \alpha^2 E^{(2)} + \dots) (\psi^{(0)} + \alpha \psi^{(1)} + \alpha^2 \psi^{(2)} + \dots) \quad (14)$$

By doing operation between two sides, and the coefficients of successive power of  $\alpha$  on both sides of this equation must be equal. We obtain the results as follows,

$$(H_0 - E^{(0)})\psi^{(0)} = 0 \quad (15)$$

$$(H_0 - E^{(0)})\psi^{(1)} = (E^{(1)} - W)\psi^{(0)} \quad (16)$$

$$(H_0 - E^{(0)})\psi^{(2)} = (E^{(1)} - W)\psi^{(1)} + E^{(2)}\psi^{(0)} \quad (17)$$

Equation (15) is the zero-order correction solution, equation (16) is the first -order correction solution and equation (17) is the second-order correction solution.

By using Equation (16), the energy and the wave function of the first order correction are as follows,

$$E_n^{(1)} = \langle \psi_n | W | \psi_n \rangle = \int_V \psi_n W \psi_n dV \quad (18)$$

$$\psi_n^{(1)} = \sum_{n \neq k} \frac{\langle \psi_k | W | \psi_n \rangle}{E_n^{(0)} - E_k^{(0)}} \psi_k^{(0)} \quad (19)$$

And if we use equation (17), we will get the result of second-order correction for energy and wave function is as follows,

$$E_n^{(2)} = \sum_{n \neq k} \frac{|\langle \psi_k | W | \psi_n \rangle|^2}{E_n^{(0)} - E_k^{(0)}} \quad (20)$$

$$\psi_n^{(2)} = \sum_{r \neq n} \left[ \sum_{m \neq n} \frac{\langle \psi_r | W | \psi_m \rangle \langle \psi_m | W | \psi_n \rangle}{(E_n^{(0)} - E_r^{(0)})(E_n^{(0)} - E_m^{(0)})} - \frac{\langle \psi_n | W | \psi_n \rangle \langle \psi_r | W | \psi_n \rangle}{(E_r^{(0)} - E_n^{(0)})^2} \right] \psi_r^{(0)} - \sum_{r \neq n} \frac{1}{2} \frac{|\langle \psi_r | W | \psi_n \rangle|^2}{(E_r^{(0)} - E_n^{(0)})^2} \psi_n^{(0)} \quad (21)$$

### 5. Result and Discussion

The vibrational energy of the hydrogen molecule ion  $H_2^+$  in the ground state which uses a harmonic oscillator is  $1/2 \hbar \omega$ , with  $\omega$  being the frequency of vibration. The amount of energy is only valid in the vibration around the point of equilibrium, i.e. 0.106 nm or  $2a_0$  (Bohr). If the vibrational motion of harassment in the form of van der Waals interactions, then the total energy can be determined using perturbation theory. In this study, the highest-order interference used is a second order. Van der Waals interactions to the vibrational hydrogen molecule ion has the form as a function of  $x$ , i.e. the distance between the electrons closest to the nucleus. The van der Waals interaction is taken into account when perturbation theory is considered as spam Hamiltonian operator, and more precisely it is the operator position of  $x$ . If the operator position of  $x$  is given on the state of vibration, it means that the van der Waals interaction is a form of vibration of the electron from the nearest core.

**Table 1.** Ground state  $1s\sigma_g$  energy  $H_2^+$ .

<b>Ground state energy without perturbation</b>	$E_0 = E_n^{(0)} = \frac{1}{2} \hbar \omega$
<b>Ground state energy with perturbation (second order)</b>	$E_0 = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} = \frac{1}{2} \hbar \omega + 0 - \lambda^2 \frac{e^4}{32\pi^2 \epsilon_0^2 m \omega^2 R^4}$

It is intended to facilitate the analytical calculations using operators, provided that the order energy correction only to the vibrational motion is zero. This means that the price expectations of the position  $x$  of the nuisance van der Waals are on the state of vibration magnitude of zero. As for the energy correction order, both have formed as the distance between the core functions of the molecule, i.e.  $R^{-4}$  as shown in Table 1. Comparison of these results with the results of other studies is shown in Table 2. In Table 2 it can be seen that the results of research Holstein has the form  $R^{-6}$  [11]

**Table 2.** Comparison correction second-order vibrational energy research results with other studies.

<b>This Research</b>	<b>Holstein</b>
$\frac{e^4}{32\pi^2\epsilon_0^2 m \omega^2 R^4}$	$\frac{e^4}{32\pi^2\epsilon_0^2 m^2 \omega^3 R^6}$

The difference is because this study used a system with one electron, that is  $H_2^+$ , while Holstein using two electrons, which is  $H_2$ . The results of a second order correction of the vibrational energy state an interaction between electrons with protons farthest, that is the pull. The negative sign in the equation indicates that the van der Waals force is an attractive force.

The equation in Table 1, was obtained vibrational energy results presented in Tables 3 and 5. According to Table 3, the vibrational energy of the hydrogen molecule ion with a harmonic oscillator in the ground state with analytical calculations result is 0.142395 eV, whereas when used with a numerical calculation by using finite difference methods the result is 0.142210 eV. By contrast, the difference of the results is 0.000185 eV. Obtained energy analytic calculation results are compared with the results of research by Fabri *et al*, the result of which can be seen in Table 4. The vibrational energy of the hydrogen molecule ion is 0.142514 eV [12], have the difference of 0.000119 eV with this research. The differences are due to the potential use of different molecules.

**Table 3.** Data ground state  $1s\sigma_g$  vibrational energy  $H_2^+$  without perturbation.

State	Vibrational frequency $\omega$	Energy without perturbation (eV)		difference(eV)
		Analytic	Numeric	
$1s\sigma_g$	2297 $cm^{-1}$	0.142395	0.142210	0.000185

This study used a harmonic oscillator potential, and on research Fabri *et al* used the Morse potential. Reason for using research Fabri *et al* as the comparison is because of the research, molecular Hamiltonian follows the Born-Oppenheimer approach as done in this study. Energy vibrational ground state is calculated from the distance the  $x$ -axis to the minimum point of the graph. Ground-state vibrational energy in a hydrogen molecule ion can be regarded as the lowest vibrational energy that occurs when the system has a temperature close to 0 K. In quantum, vibration will always be there and never be stopped even at the lowest state though. It is a consequence of the Heisenberg uncertainty, which is a fundamental principle in quantum mechanics.

**Table 4.** Comparison of vibrational energy to other studies the results.

<b>This research (eV)</b>	<b>Fabri <i>et al</i> (eV)</b>	<b>Difference (eV)</b>
0.142395	0.142514	0.000119

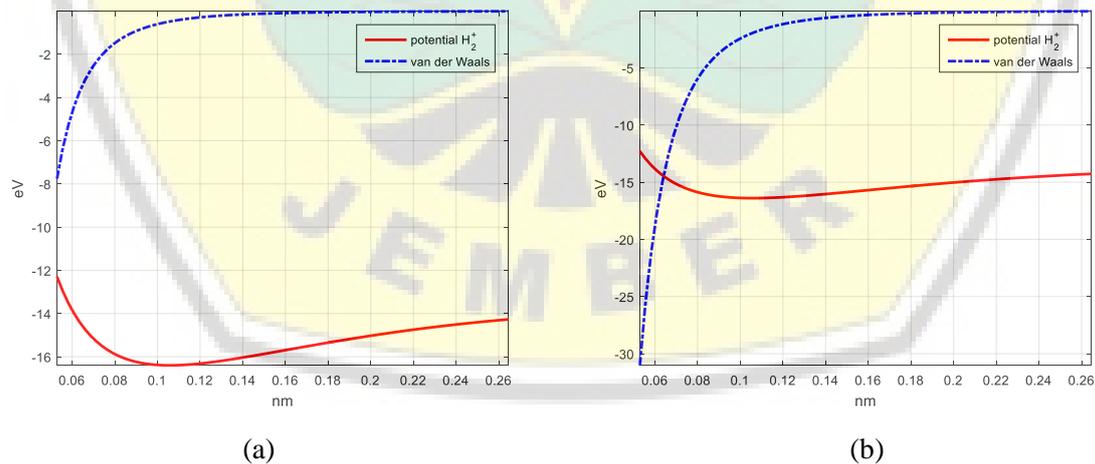
Further results of a second order vibrational energy correction due to the van der Waals interaction can be seen in Table 5. The independent variable in the table is the distance between the core molecule and parameters. The distances between the nuclei of the molecules used are  $2.00a_0$ ;  $2.25a_0$ ;  $2.50a_0$  and  $2.75a_0$  and parameters  $1 \times 10^{-3}$ ;  $2 \times 10^{-3}$  and  $3 \times 10^{-3}$ . From Table 5, it can be interpreted that the greater the distance between the nuclei of the molecule, the smaller the vibrational energy correction second order, which means the total vibrational energy is close to the value of the vibrational energy

without perturbation, and *vice versa*. That is because that the correction of the second order vibrational energy has the form  $R^{-4}$  as shown in Table 1. While the parameters used when greater, then the order of two vibrational energy correction (van der Waals) produced greater, so the total vibrational energy has a big difference, compared to the vibrational energy without perturbation.

**Table 5.** Second-order correction of energy and total energy corrected order of two to three different parameters.

$R (a_0)$	$E_0^{(2)}(eV)$			$E_0 = E_0^{(0)} - E_0^{(2)}(eV)$		
	$\lambda=1 \times 10^{-4}$	$\lambda=2 \times 10^{-4}$	$\lambda=3 \times 10^{-4}$	$\lambda=1 \times 10^{-4}$	$\lambda=2 \times 10^{-4}$	$\lambda=3 \times 10^{-4}$
<b>2.00</b>	0.006081	0.024324	0.054730	0.136313	0.118070	0.087664
<b>2.25</b>	0.003797	0.015190	0.034179	0.138597	0.127204	0.108215
<b>2.50</b>	0.002491	0.009966	0.022424	0.139903	0.132428	0.119970
<b>2.75</b>	0.001701	0.006806	0.015315	0.140693	0.135588	0.127079

The parameters used in this study has been arranged, so that the correction of the second order vibrational energy (van der Waals) value does not exceed the vibrational energy without interruption. If the value of second-order correction of the vibrational energy is greater than the energy vibration without perturbation, then the vibrational movement becomes dominant again. It can be seen in Figure 3 (a) and 3 (b). From both images, it can be interpreted that the larger parameters used, the greater the van der Waals energy is generated and the curvature of the potential graph becomes invisible. Impacts are not dominant vibrational motion become more physically meaningful vibrational motion of molecules  $H_2^+$  becomes unobservable. Therefore, the parameters used to be worth very little, so that the vibrational motion of molecules  $H_2^+$  can still be observed.



**Figure 1.** Graph van der Waals energy potential and the hydrogen molecular ion  $H_2^+$  with parameters (a)  $\lambda=0.0001$  and (b)  $\lambda=0.0002$ .

Then the results of research on the molecular vibrational wave functions  $H_2^+$  either without interruption or with disorders such as van der Waals interactions can be seen in Table 6. In quantum mechanics, the state of a system is described or represented by a wave function. The wave function contains all the information about the state of the system at any time and cannot be measured directly. According to Max Born, the wave function does not have any physical meaning. The function will be significant when multiplied by the wave function that generates adjacent density probability. In this

study, the vibrational wave function is only simulated with Matlab. In perturbation theory, the total wave function is a superposition of the wave-function undisturbed and disturbed wave function to a particular order. This study used the highest order is second order. The function of the parameters on the total vibrational wave function is equal to the total vibrational energy, i.e. as a controller, so that the value is not enlarged.

## 6. Conclusion

Based on the results, the following conclusions are drawn. (1) The energy vibration of the hydrogen molecular ion  $H_2^+$  in the ground state with van der Waals interactions disturbance magnitude depends on the distance between the core molecule  $H_2^+$  and parameter  $\lambda$  used. The greater the distance between the nuclei of molecules, the lower (towards minus) vibrational energy is, and *vice versa*. Meanwhile, the larger parameters are, the greater the intruder energy is, and *vice versa*. The amount of molecular vibrational energy  $H_2^+$  disturbed ranges from 0.087664 to 0.140693 eV; (2) In general, ground-state vibrational wave functions disrupted basic shape that resembles the vibration of the ground state wave function without interruption, the harmonic oscillator wave functions. The shape varies depending on the magnitude of the distance between the core molecule  $H_2^+$  and parameters. The present study also obtained another conclusion that if the van der Waals energy is greater than the energy of vibration, the vibrational motion of molecules become visible again. It is also that the van der Waals interaction disorders in vibrational motion  $H_2^+$  can shift the equilibrium point becomes greater.

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