A Theoretical Study on Vibrational Energies of Molecular Hydrogen and Its Isotopes Using a Semi-classical Approximation

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Abstract: *This study aims to apply a semi-classical approach using some analytically solvable potential functions to accurately compute the first ten pure vibrational energies of molecular hydrogen (H_2) and its isotopes in their ground electronic states. This study also aims at comparing the accuracy of the potential functions within the framework of the semi-classical approximation. The performance of the approximation was investigated as a function of the molecular mass. In this approximation, the nuclei were assumed to move in a classical potential. The Bohr-Sommerfeld quantization rule was then applied to calculate the vibrational energies of the molecules numerically. The results indicated that the first vibrational transition frequencies ($\nu_{1\leftarrow0}$) of all hydrogen isotopes were consistent with the experimental ones, with a minimum percentage error of 0.02% for ditritium (T_2) molecule using the Modified-Rosen-Morse potential. It was also demonstrated that, in general, the Rosen-Morse and the Modified-Rosen-Morse potential functions were better in terms of calculating the vibrational energies of the molecules than Morse potential. Interestingly, the Morse potential was found to be better than the Manning-Rosen potential. Finally, the semi-classical approximation was found to perform better for heavier isotopes for all potentials applied in this study.*

Keywords: *semi-classical approximation; classical potential functions; hydrogen isotopes; Bohr-Sommerfeld quantization*

INTRODUCTION

The molecular hydrogen (H_2) and its isotopes are of great importance in molecular quantum chemistry. The fact that the experimental energies of the systems are consistent with their corresponding theoretical values has long been considered an initial platform for testing and developing the practical techniques and theoretical models [1-2].

Exact experimental vibrational levels for H_2 and deuterium-bearing hydrogen molecules, i.e., hydrogen deuteride (HD) and dideuterium (D_2) have been widely reported in the literature [3-5]. On the other hand, physical properties of the tritium-bearing hydrogen molecules, i.e., tritiated hydrogen (HT), deuterium-tritium (DT), and ditritium (T_2), have been less frequently measured. The reason was due to the stringent safety requirements to hold the radioactive species, which results in limited access and handling difficulty in the experimental study of these systems [6]. Some of the empirical studies on the first vibrational frequencies for these systems were reported for T_2 molecule [7], DT molecule [8], and the most recent one for HT, DT, and T_2 molecules [6]. With these recent experimental reports, theoretical models to study the systems, especially for the fundamental tone, can be tested for all molecular hydrogen isotopes.

From the theoretical point of view, highly accurate energy calculations of isotopes of molecular hydrogen have also been thoroughly performed. Various types of theoretical calculations have been developed, including the moment constant summability method [9], free-complement variational theory [10-11] and matrix Numerov method [12] for the H_2 molecule. The non-relativistic calculations were also reported on energy levels of D_2 molecule [13] and of HD molecule [14]. Similarly, a theoretical study on vibrational energy levels of the hydrogen molecule and its isotopes was presented [15]. Besides, highly accurate ab-initio calculations have also been extended to investigate the effects of vibrations on the chemical and physical properties of other quantum systems. These studies include the use of the first-principle DFT calculation to investigate vibrational effects on vacancies in silicon [16], nitrogen-doped diamond [17], germanene [18], monolayer hexagonal boron nitride [19]. DFT also was used to investigate the potential of halogen-substituted N-methyl-4-piperidones curcumin analog compounds as candidates for optoelectronic materials [20]. First-principle vibrational free energy calculations have also been conducted to study defects in silicon [21-22].

Moreover, DFT was used along with ab-initio correlated wavefunction theory (WFT) methods to obtain highly accurate potential energy curves (PECs) of fluorine adsorption on coronene [23], setting up a high-level benchmark for theoretical studies on graphene functionalization. The results generated from the above-mentioned first-principle calculations are in excellent agreement with their corresponding experimental values and other ab-initio products. These findings indicate that DFT and correlated WFT are among the most accurate theoretical methods. Therefore, they are recommended for performing precise high calculations on rovibrational, electronic, structural, optical, and other properties of materials for investigating their potential use in devices.

Recently, the semi-classical method has been applied to study the vibrational states of molecules [24-25]. One approach in this method is to use the Bohr-Sommerfeld quantization rule. One can apply the potential analytical surfaces such as the Morse potential rather than applying a more complex ab-initio potential. Despite being simple, the Morse potential has been proven accurate in studying the diatomic molecules [26-27]. In our previous study [28], we have successfully applied a semi-classical approach using the Morse potential [29] to calculate the vibrational energies of the molecular H_2. In this study, we observed that 10 out of 15 vibrational levels of H_2 could be generated with reasonable accuracy. In addition to the Morse potential, there have also been other analytically solvable potentials, including the Rosen-Morse [30], Manning-Rosen [31], and the Modified-Rosen-Morse potential [32]. These potentials have been extensively applied to study the interactions in molecules. However, they have not been explored to calculate the vibrational energies of molecular hydrogen isotopes within the framework of the semi-classical approximation.

Since their introduction, most of the potential functions have been widely explored and compared for their performance in describing the molecular interaction of diatomic molecules. Consequently, a variety of claims have been drawn by different researchers that a particular potential is better than the others or vice versa. For instance, Deng and Fan [33] claimed that the Deng-Fan potential was better than Morse potential in describing the interactions of diatomic molecules. Moreover, Liu et al. [34] reported that vibrational levels predicted by Manning-Rosen potential model were better than those predicted by the Morse potential model for a $^3\Sigma_u^+$ of the Li_2 molecule. Wang et al. [35] made a contradictory claim that the Morse potential was better than Deng-Fan, Manning-Rosen, and the Schiöberg potential in describing the interaction of diatomic molecules. Therefore, more comprehensive theoretical studies on different chemical-physical properties of various diatomic molecules using these potentials are crucial in testing the accuracy of the potentials.

This present paper aims to apply the semi-classical method using the Morse, Manning-Rosen, Rosen-Morse, and the modified Rosen-Morse potential to calculate the first 10 vibrational energies of molecular H_2 and its isotopes (HD, HT, D_2, DT, and T_2) in their ground electronic state $X\Sigma_g^+$. Also, the accuracy of the calculation in the framework of the semi-classical approximation was examined. Finally, the performance of the approximation was evaluated as a function of the molecular mass.

■ COMPUTATIONAL METHODS

The Semi-Classical Approximation Using Analytically Solvable Potentials

The semi-classical method used in this article was applied within the framework of the Born-Oppenheimer approximation. In this approximation, the nuclei and electrons were assumed to move independently. The further assumption would be that the vibrational and the rotational motion were separated. Therefore the vibrational bound states of the molecular hydrogen isotopes can be obtained by solving the time-independent Schrödinger equation for the nuclei shown in Eq. (1):

$$\left(\hat{T}+\hat{V}\right)\left|\Psi\right\rangle = E_n\left|\Psi\right\rangle \tag{1}$$

In the semi-classical approximation, one does not need to solve Eq. (1) directly for E_n but needs to assume that the nuclei move in a classical potential V(r) and then apply the Bohr-Sommerfeld quantization rule to approximate vibrational energy eigenvalues E_n. Hence, using the quantization rule led to dimensionless action S at a particular energy E_n [36]:

$$S(E_n)=\left(\frac{2\mu}{\hbar^2}\right)^{1/2}\int_{r_{in}}^{r_{out}}\left(E_n-V(r)\right)^{1/2}dr-\left(n+\frac{1}{2}\right)\pi \tag{2}$$

Despite $S(E_n)$ is dimensionless, all other quantities contained in $S(E_n)$ still have their standard units. All physical quantities were defined in a way that they are dimensionless. Therefore, Eq. (2) can be written as:

$$s(\varepsilon_n)=\gamma\int_{x_{in}}^{x_{out}}\left(\varepsilon_n-v(x)\right)^{1/2}dx-\left(n+\frac{1}{2}\right)\pi \tag{3}$$

where $s(\varepsilon_n)$ is the new dimensionless action. All other unknown dimensionless quantities defined to arrive at Eq. (3) are described as follows. Firstly, dimensionless position x was defined as $x \equiv r/\delta$. Here, δ is a parameter with the dimension of length introduced to make position x dimensionless. This δ parameter also appeared in the potential functions as shown in Eq. (8) to Eq. (11). This parameter has a physical meaning of controlling the width of the potential functions. Hence, it has to be fitted to experimental values for given energy using a particular potential function. Similarly, γ is a dimensionless quantity introduced to make the constants just before the integral in Eq. (2) dimensionless and to account for δ and equilibrium potential D_e in the calculation. This γ value, shown in Eq. (4), represents the quantum nature of the problem where more significant matters of *γ* correspond to systems with a more negligible quantum effect. In other words, the systems behave more classically for larger γ and vice versa.

$$\gamma=\left(\frac{2\mu D_e\delta^2}{\hbar^2}\right)^{1/2} \tag{4}$$

Here, D_e is the potential at the equilibrium position r_e, and μ is the reduced mass of the nuclei. Secondly, x_{in} and x_{out} in Eq. (3) are the scaled classical turning points obtained by first solving r_{in} and r_{out} using:

$$V(r_{in})=V(r_{out})=E_n \tag{5}$$

Next, ε_n in Eq. (3) is the scaled vibrational energy for a particular vibrational quantum state n, defined as

$$\varepsilon_n \equiv \frac{E_n}{D_e} \tag{6}$$

Finally, v(x) in Eq. (3) is the scaled classical potential governing the motion of the nuclei. This v(x) function can be determined from v(r), which was defined as

$$v(r)\equiv\frac{V(r)}{D_e} \tag{7}$$

In this article, the potential functions used were the Morse potential $V_M(r)$ [29] shown in Eq. (8). The Manning-Rosen potential $V_{MR}(r)$ in the form presented in [35] as shown in Eq. (9). The Rosen-Morse potential $V_{RM}(r)$ in the form presented in [37] as shown in Eq. (10), and the modified Rosen-Morse potential $V_{MRM}(r)$ [32] demonstrated in Eq. (11). It was important to note that there was a slight change in each equation where $-D_e$ was added, which only yielded $-D_e$ at the potential minimum but did not affect the physical properties of the potentials at all. It is also important to note that the bond length r_e used in this article was taken as a pre-computed parameter.

$$V_M(r)=D_e\left(\left(1-e^{-(r-r_e)/\delta}\right)^2-1\right) \tag{8}$$

$$V_{MR}(r)=D_e\left(\left(1-\frac{e^{r_e/\delta}-1}{e^{r/\delta}-1}\right)^2-1\right) \tag{9}$$

$$V_{RM}(r) = D_e\left(\left(1-\frac{e^{2r_e/\delta}+1}{e^{2r/\delta}+1}\right)^2-1\right) \tag{10}$$

$$V_{MRM}(r) = D_e\left(\left(1-\frac{e^{2(r_e-r_{ij})/\delta}+1}{e^{2(r-r_{ij})/\delta}+1}\right)^2-1\right) \tag{11}$$

Computational Details

Overall, the computational details used in this research followed the same procedures described in [28]. Calculation of the vibrational energies of the molecular hydrogen isotopes was done by solving Eq. (3) numerically. The numerical methods used in calculating the vibrational energies in Eq. (3) were numerical integration using the Simpson's rule and root finding using the false position method, with 1024 divisions and a tolerance of 10^{-7}. The steps involved are as follows. First, the dimensionless quantity γ was determined using Eq. (4). Second, the classical turning points were determined for all potentials using Eq. (5). After that, γ values, classical turning points, and the potential functions were substituted into Eq. (3). Finally, Eq. (3) was solved numerically to obtain the pure vibrational energies of the molecules. In this final step, the value of δ was varied to get the first vibrational energy which can match its experimental value. This δ value was then used to solve the higher vibrational energy levels of the molecules.

■ RESULTS AND DISCUSSION

Physical Constants Used in the Calculation

Reduced mass μ of nuclei of the molecules were 0.50391261 a.m.u., 0.67171137 a.m.u., 0.75540394 a.m.u., 1.00705111 a.m.u., 1.20764393 a.m.u., and 1.50802486 a.m.u., for H_2, HD, HT, D_2, DT and T_2 respectively [38]. The bond length value used in the calculation for all molecules in this study was 0.74142 Å [38]. Using an experimental value for D_e = 38287 cm^{-1} and the reduced mass of the molecules, the values of the dimensionless quantity γ of the molecules were calculated using Eq. (4), and they were found to be 33.830δ, 39.059δ, 41.421δ, 47.825δ, 52.372δ, and 58.524δ respectively, where δ in Å.

Classical Turning Points

The classical turning points for the Morse potential (M) had been presented before in [28], from which the classical turning points were

$$r_{in(M)} = r_e - \delta\ln\left(1+\sqrt{\varepsilon_n+1}\right) \tag{12a}$$

$$r_{out(M)} = r_e - \delta\ln\left(1-\sqrt{\varepsilon_n+1}\right) \tag{12b}$$

Using similar procedures, i.e., by applying Eq. (5) to Eq. (9), (10), and (11), the classical turning points for the Manning-Rosen (MR), Rosen-Morse (RM), and the Modified-Rosen-Morse (MRM) potentials were derived and respectively shown in Eq. (13), (14) and (15).

$$r_{in(MR)} = \delta\ln\left(1+\frac{e^{r_e/\delta}-1}{1+\sqrt{\varepsilon_n+1}}\right) \tag{13a}$$

$$r_{out(MR)} = \delta\ln\left(1+\frac{e^{r_e/\delta}-1}{1-\sqrt{\varepsilon_n+1}}\right) \tag{13b}$$

$$r_{in(RM)} = \frac{\delta}{2}\ln\left(\frac{e^{2r_e/\delta}+1}{1+\sqrt{\varepsilon_n+1}}-1\right) \tag{14a}$$

$$r_{out(RM)} = \frac{\delta}{2}\ln\left(\frac{e^{2r_e/\delta}+1}{1-\sqrt{\varepsilon_n+1}}-1\right) \tag{14b}$$

$$r_{in(MRM)} = r_{ij}+\frac{\delta}{2}\ln\left(\frac{e^{2(r_e-r_{ij})/\delta}+1}{1+\sqrt{\varepsilon_n+1}}-1\right) \tag{15a}$$

$$r_{out(MRM)} = r_{ij}+\frac{\delta}{2}\ln\left(\frac{e^{2(r_e-r_{ij})/\delta}+1}{1-\sqrt{\varepsilon_n+1}}-1\right) \tag{15b}$$

For the Modified-Rosen-Morse potential, r_{ij} values were calculated using Eq. (16) [32].

$$r_{ij} = r_e - \sqrt{\frac{KD_e}{k_e}} \tag{16}$$

where K is a dimensionless constant given by

$$K = \frac{d^2v(r)}{dr'^2}\bigg|_{r'=1};\; r' = \frac{r-r_{ij}}{r_e-r_{ij}} \tag{17}$$

Vibrational Energy Levels of H_2, HD, HT, D_2, DT, and T_2 Molecules

The calculated first ten vibrational energies for the molecular hydrogen and its isotopes in their ground electronic state $X\Sigma_g^+$ are presented in this section. Eq. (3) was numerically evaluated using values given in the previous section. The equation had already been solved for the H_2 molecule using the Morse potential in our earlier study [28], but it was recalculated in this research using the most recent experimental values to obtain the results comparable to that of the hydrogen isotopes calculated in this study. The most recent experimental values used here were 36118.06962 cm^{-1} [39], 36405.78366 cm^{-1} [40], and 36748.36286 cm^{-1} [3] for the first vibrational energy levels of H_2, HD, and D_2, respectively. Meanwhile, the most recent theoretical values for the first vibrational energy levels for HT, DT, and T_2 were 36512.19957 cm^{-1}, 36881.2812 cm^{-1}, and 37028.49625 cm^{-1} [41], respectively. Values of δ matching the corresponding experimental first vibrational levels for H_2, HD, HT, D_2, DT, and T_2 are shown in Table 1. These δ values were then used to calculate the first ten vibrational energy levels for all molecules. For the Modified-Rosen-Morse potential, the r_{ij} values used are also presented in Table 1, calculated using Eq. (16) and (17) based on diatomic constants adapted from [38]. Calculated results of the first ten vibrational energies of the molecules are presented in Table 2.

It is evident from Table 2 that our calculated energies using Rosen-Morse and Modified Rosen Morse potential functions were consistent with the corresponding energies reported in [42], with errors below 1% for all molecules. Similarly, the results for the first 5 vibrational energy levels for all molecules were also in good agreement when using the Morse potential (error below 1%). Still, for sizeable vibrational quantum numbers, it was clear that the difference between the calculation and the experimental data became significant. On the other hand, only the first three vibrational levels with errors of less than 1% could be generated using the Manning-Rosen potential. For H_2 molecule with $n = 9$, the use of Manning-Rosen potential resulted in a much higher percentage of error compared to that of the Morse, Rosen-Morse, and Modified Rosen Morse potential, with up to 54.81% of error compared to 12.83%, 0.47% and 0.17% for the respective potential functions. The accuracy of these potential functions within the framework of the semi-classical approximation is discussed further in the following section.

It is also clear from Table 2 that for any vibrational level calculated using any potential function, isotopic shifts in vibrational energies occurred when other isotopes substituted one atom or both atoms. The reason was due to the difference in the reduced mass of the molecules containing different isotopes, which leads to the increase or decrease in the corresponding calculated energy. The substitution of an atom or both atoms with heavier isotopes led to the lower vibrational energies and hence results in more chemically stabilized vibrational states. This stabilization, in addition to some other factors explained in the next section, led to more accurate vibrational levels for heavier molecules.

Regarding the dissociation energy, it is clear that any change to the molecule with heavier isotopes led to a higher bond dissociation energy of the molecule. Therefore, the chemical bond of such molecules became more muscular, which eventually affects the molecules' behavior in any chemical reaction, which involves bond cleavage. The stronger the chemical bond between isotopes, the higher the energy required to break the chemical bond within the molecule from its first vibrational state into its unexcited constituent atoms/isotopes. As chemical reactions between two atoms

Table 1. Values of δ and r_{ij} used in the calculation

Molecule	δ_M (Å)	δ_{MR} (Å)	δ_{RM} (Å)	δ_{MRM} (Å)	r_{ij} (Å)
H_2	0.71715238100	0.97932457700	0.92625240460	0.92405655150	0.01480561
HD	0.71734847950	0.98070005400	0.92634829660	0.92411931120	0.01500609
HT	0.71743336176	0.98123423230	0.92639796470	0.92412744480	0.01527452
D_2	0.71765735300	0.98249317680	0.92654899188	0.92426980660	0.01531373
DT	0.71780750840	0.98325158400	0.92666155500	0.92436195030	0.01543833
T_2	0.71800402150	0.98415409740	0.92682071850	0.92451846200	0.01544307

Table 2. Calculated energies with % errors[‡] for first 10 vibrational energies of the molecules using the Morse (M), Manning-Rosen (MR), Rosen-Morse (RM), and Modified-Rosen-Morse (MRM) potentials. Calculated energies from ab-initio methods in [42][‡] are also presented

Molecule	n	$E_{n(M)}$/cm^{-1} (% error)	$E_{n(MR)}$/cm^{-1} (% error)	$E_{n(RM)}$/cm^{-1} (% error)	$E_{n(MRM)}$/cm^{-1} (% error)	$E_n^{\ddagger}$/cm^{-1}
H_2	0	-36118.070 (0.00)	-36118.070 (0.00)	-36118.070 (0.00)	-36118.070 (0.00)	-36118.074
	1	-31969.921 (0.04)	-32085.512 (0.40)	-31941.486 (0.05)	-31940.867 (0.05)	-31956.927
	2	-28074.723 (0.16)	-28427.373 (1.41)	-27984.898 (0.16)	-27982.911 (0.17)	-28031.088
	3	-24432.479 (0.40)	-25108.677 (3.18)	-24254.567 (0.33)	-24250.572 (0.35)	-24335.689
	4	-21043.186 (0.84)	-22098.637 (5.90)	-20757.141 (0.53)	-20750.621 (0.56)	-20867.698
	5	-17906.847 (1.59)	-19370.069 (9.89)	-17499.678 (0.72)	-17490.265 (0.77)	-17626.119
	6	-15023.460 (2.81)	-16898.893 (15.65)	-14489.684 (0.84)	-14477.179 (0.92)	-14612.257
	7	-12393.027 (4.76)	-14663.724 (23.95)	-11735.138 (0.80)	-11719.538 (0.93)	-11830.105
	8	-10015.546 (7.85)	-12645.513 (36.17)	-9244.540 (0.46)	-9226.068 (0.66)	-9286.901
	9	-7891.020 (12.83)	-10827.248 (54.81)	-7026.942 (0.47)	-7006.079 (0.17)	-6993.907
HD	0	-36405.784 (0.00)	-36405.784 (0.00)	-36405.784 (0.00)	-36405.784 (0.00)	-36405.778
	1	-32785.512 (0.04)	-32873.724 (0.31)	-32763.984 (0.03)	-32763.511 (0.03)	-32773.635
	2	-29354.790 (0.12)	-29627.277 (1.05)	-29286.222 (0.11)	-29284.694 (0.12)	-29318.920
	3	-26113.619 (0.29)	-26643.017 (2.32)	-25976.499 (0.24)	-25973.402 (0.25)	-26038.161
	4	-23061.999 (0.58)	-23899.984 (4.24)	-22839.027 (0.39)	-22833.925 (0.41)	-22928.893
	5	-20199.930 (1.05)	-21379.384 (6.95)	-19878.246 (0.56)	-19870.791 (0.60)	-19989.738
	6	-17527.412 (1.78)	-19064.321 (10.71)	-17098.829 (0.71)	-17088.776 (0.77)	-17220.515
	7	-15044.445 (2.89)	-16939.573 (15.85)	-14505.710 (0.80)	-14492.927 (0.89)	-14622.386
	8	-12751.029 (4.53)	-14991.400 (22.90)	-12104.090 (0.77)	-12088.577 (0.90)	-12198.059
	9	-10647.165 (6.98)	-13207.369 (32.71)	-9899.461 (0.53)	-9881.364 (0.71)	-9952.060
HT	0	-36512.200 (0.00)	-36512.200 (0.00)	-36512.200 (0.00)	-36512.200 (0.00)	-36512.166

Table 2. Calculated energies with % errors‡ for first 10 vibrational energies of the molecules using the Morse (M), Manning-Rosen (MR), Rosen-Morse (RM), and Modified-Rosen-Morse (MRM) potentials. Calculated energies from ab-initio methods in [42]‡ are also presented (*Continued*)

Molecule	n	$E_{n(M)}$/cm^{-1} (% error)	$E_{n(MR)}$/cm^{-1} (% error)	$E_{n(RM)}$/cm^{-1} (% error)	$E_{n(MRM)}$/cm^{-1} (% error)	$E_n^{\ddagger}$/cm^{-1}
	1	-33088.949 (0.04)	-33167.879 (0.27)	-33069.743 (0.02)	-33069.314 (0.02)	-33077.320
	2	-29834.167 (0.11)	-30079.091 (0.93)	-29772.814 (0.09)	-29771.425 (0.10)	-29800.557
	3	-26747.854 (0.26)	-27225.971 (2.05)	-26624.747 (0.20)	-26621.924 (0.21)	-26678.870
	4	-23830.010 (0.51)	-24590.639 (3.71)	-23629.042 (0.34)	-23624.377 (0.36)	-23710.043
	5	-21080.637 (0.90)	-22156.968 (6.05)	-20789.374 (0.49)	-20782.532 (0.53)	-20892.705
	6	-18499.733 (1.50)	-19910.379 (9.24)	-18109.606 (0.64)	-18100.334 (0.69)	-18226.406
	7	-16087.298 (2.39)	-17837.669 (13.53)	-15593.795 (0.75)	-15581.935 (0.83)	-15711.716
	8	-13843.334 (3.69)	-15926.855 (19.30)	-13246.209 (0.78)	-13231.709 (0.89)	-13350.363
	9	-11767.839 (5.58)	-14167.046 (27.11)	-11071.339 (0.66)	-11054.266 (0.82)	-11145.411
D_2	0	-36748.363 (0.00)	-36748.363 (0.00)	-36748.363 (0.00)	-36748.363 (0.00)	-36748.349
	1	-33765.748 (0.03)	-33825.769 (0.21)	-33751.239 (0.01)	-33750.915 (0.01)	-33754.742
	2	-30909.347 (0.09)	-31097.461 (0.70)	-30862.703 (0.06)	-30861.650 (0.06)	-30880.242
	3	-28179.160 (0.20)	-28550.209 (1.52)	-28084.890 (0.13)	-28082.738 (0.14)	-28122.759
	4	-25575.189 (0.37)	-26171.943 (2.71)	-25420.029 (0.24)	-25416.448 (0.25)	-25480.643
	5	-23097.432 (0.63)	-23951.635 (4.35)	-22870.443 (0.36)	-22865.149 (0.38)	-22952.701
	6	-20745.889 (1.01)	-21879.188 (6.53)	-20438.557 (0.49)	-20431.313 (0.52)	-20538.231
	7	-18520.562 (1.55)	-19945.349 (9.37)	-18126.900 (0.60)	-18117.528 (0.66)	-18237.066
	8	-16421.450 (2.32)	-18141.622 (13.03)	-15938.116 (0.69)	-15926.497 (0.77)	-16049.615
	9	-14448.553 (3.37)	-16460.195 (17.77)	-13874.962 (0.73)	-13861.047 (0.83)	-13976.943
DT	0	-36881.281 (0.00)	-36881.281 (0.00)	-36881.281 (0.00)	-36881.281 (0.00)	-36881.271
	1	-34148.713 (0.03)	-34199.145 (0.18)	-34136.568 (0.00)	-34136.296 (0.00)	-34137.946

Table 2. Calculated energies with % errors[‡] for first 10 vibrational energies of the molecules using the Morse (M), Manning-Rosen (MR), Rosen-Morse (RM), and Modified-Rosen-Morse (MRM) potentials. Calculated energies from ab-initio methods in [42][†] are also presented (*Continued*)

Molecule	n	$E_{n(M)}$/cm^{-1} (% error)	$E_{n(MR)}$/cm^{-1} (% error)	$E_{n(RM)}$/cm^{-1} (% error)	$E_{n(MRM)}$/cm^{-1} (% error)	$E_n^{\dagger}$/cm^{-1}
	2	-31521.306 (0.09)	-31680.242 (0.59)	-31482.126 (0.04)	-31481.236 (0.04)	-31494.199
	3	-28999.061 (0.18)	-29314.359 (1.26)	-28919.567 (0.10)	-28917.744 (0.11)	-28948.381
	4	-26581.978 (0.31)	-27092.105 (2.24)	-26450.569 (0.18)	-26447.526 (0.19)	-26499.146
	5	-24270.057 (0.52)	-25004.835 (3.56)	-24076.875 (0.28)	-24072.356 (0.30)	-24145.463
	6	-22063.298 (0.81)	-23044.578 (5.29)	-21800.294 (0.39)	-21794.084 (0.42)	-21886.630
	7	-19961.700 (1.21)	-21203.979 (7.51)	-19622.710 (0.50)	-19614.630 (0.55)	-19722.304
	8	-17965.265 (1.77)	-19476.236 (10.33)	-17546.081 (0.60)	-17535.999 (0.66)	-17652.523
	9	-16073.991 (2.53)	-17855.059 (13.89)	-15572.444 (0.67)	-15560.275 (0.75)	-15677.744
T_2	0	-37028.496 (0.00)	-37028.496 (0.00)	-37028.496 (0.00)	-37028.496 (0.00)	-37028.481
	1	-34574.579 (0.03)	-34615.299 (0.15)	-34564.814 (0.00)	-34564.595 (0.00)	-34563.983
	2	-32204.784 (0.08)	-32333.895 (0.48)	-32173.161 (0.02)	-32172.445 (0.02)	-32179.461
	3	-29919.112 (0.15)	-30176.855 (1.01)	-29854.684 (0.06)	-29853.213 (0.07)	-29873.687
	4	-27717.562 (0.26)	-28137.285 (1.78)	-27610.570 (0.13)	-27608.104 (0.14)	-27645.628
	5	-25600.134 (0.41)	-26208.789 (2.80)	-25442.044 (0.21)	-25438.369 (0.22)	-25494.449
	6	-23566.830 (0.63)	-24385.422 (4.12)	-23350.378 (0.30)	-23345.302 (0.32)	-23419.519
	7	-21617.648 (0.92)	-22661.653 (5.79)	-21336.886 (0.39)	-21330.245 (0.42)	-21420.429
	8	-19752.589 (1.31)	-21032.333 (7.87)	-19402.931 (0.48)	-19394.591 (0.53)	-19497.002
	9	-17971.653 (1.83)	-19492.660 (10.44)	-17549.922 (0.56)	-17539.781 (0.62)	-17649.309

[‡] Percentage errors in our results were calculated based on ab initio results in [42]

occur when the chemical bond is cleaved, molecules with heavier isotopes would undergo slower chemical reactions. The reason is that the amount of energy required to cleave the chemical bond in the molecules with heavier isotopes is more significant than those of the lighter isotopes. It can also be inferred from Table 2 that molecules with heavier isotopes tend to have more dense vibrational states, which can be seen from the smaller spacing between their adjacent states compared to the lighter ones. These findings indicate that the energy required to excite a molecule with heavier isotopes from a particular state into its next vibrational level is lower than that of the molecule with lighter isotopes. This argument has long been used in spectroscopic studies to infer the previously unknown heavy isotopes in a mix of diatomic molecules with different isotopes.

Fig. 1 illustrates the comparison of the first ten energy levels between our results using the Morse and Modified Rosen Morse potentials and those obtained from the ab-initio calculations [42] for the H_2 molecule. The forms of the potential functions were also plotted in the exact figure. It is evident from Fig. 1(a) that the difference between our results and ab-initio results [42] became more apparent for higher vibrational states using the Morse potential. The large discrepancy at higher vibrational states was significantly reduced by using the modified Rosen-Morse potential function, as shown in Fig. 1(b). This finding is a clear indication that the modified Rosen-Morse potential was a better potential function than the Morse potential.

Accuracy of the Semi-classical Approximation

Comparison with experimental values and literature

In most of the reported literature, the experimental data are not fully available for all vibrational energies of the molecules. The only complete data available for the molecules are the first vibrational transition frequencies ($v_{1\leftarrow 0}$). Therefore, the accuracy of our calculations was assessed using these experimental values as shown in Table 3. As can be seen from Table 3, for the first transition frequencies, our analyses are in good agreement with the most accurate and recent corresponding experimental values. The most accurate results from our calculations came from the use of Rosen-Morse and the Modified-Rosen-Morse potential.

Based on Table 3, the errors resulted from the calculation of vibrational frequencies of molecular hydrogen isotopes using the Morse potential were significantly lower than those from the Manning-Rosen potential, indicating that the Morse potential was much better than the Manning-Rosen potential. This result also implied that the Morse potential was also better than the Deng-Fan potential and Schiöberg potential in describing some diatomic molecular interactions as it had been previously proven in [35] that despite being different in their initial forms, Manning-Rosen, Deng-Fan, and the Schiöberg potentials were empirically the same. Our finding agrees with the study by Wang et al. [35] where the calculations of anharmonicity $\omega_e\chi_e$ and vibrational rotational coupling parameter α_e for 16 diatomic molecules were conducted, and the results were compared to the experimental values. The authors indicated that the classic Morse potential was better than the Deng-Fan, Manning-Rosen, and the Schiöberg potential. This finding

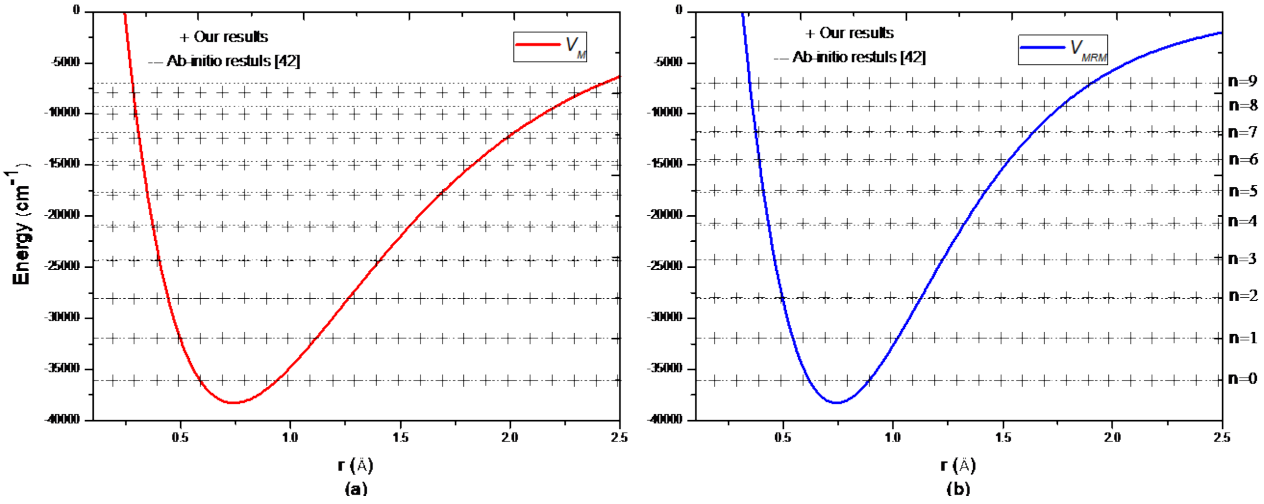


Fig 1. (a) First 10 vibrational energies of H_2 molecule using the Morse potential V_M and (b) Modified Rosen-Morse potential V_{MRM}. Energies from ab-initio results [42] are also shown

Table 3. First vibrational frequencies $\nu_{1\leftarrow 0}$ ($\Delta J=0$) with % errors[‡] using the Morse (M), Manning-Rosen (MR), Rosen-Morse (RM), and Modified-Rosen-Morse (MRM) potentials. Exact and accurate corresponding values from the most recent experiments are also presented

Molecule	$v_{1\leftarrow 0(M)}$ in cm^{-1} (% error)	$v_{1\leftarrow 0(MR)}$ in cm^{-1} (% error)	$v_{1\leftarrow 0(RM)}$ in cm^{-1} (% error)	$v_{1\leftarrow 0(MRM)}$ in cm^{-1} (% error)	$v_{1\leftarrow 0}$ in cm^{-1} (exp.)
H_2	4148.149 (0.31)	4032.557 (3.09)	4176.583 (0.37)	4177.203 (0.39)	4161.166[a]
HD	3620.272 (0.33)	3532.060 (2.76)	3641.799 (0.27)	3642.273 (0.28)	3632.161[a]
HT	3423.251 (0.34)	3344.321 (2.63)	3442.456 (0.22)	3442.885 (0.24)	3434.812[b]
D_2	2982.615 (0.37)	2922.593 (2.37)	2997.124 (0.12)	2997.448 (0.13)	2993.617[a]
DT	2732.568 (0.39)	2682.136 (2.23)	2744.713 (0.05)	2744.986 (0.06)	2743.342[b]
T_2	2453.917 (0.43)	2413.197 (2.08)	2463.682 (0.03)	2463.901 (0.02)	2464.504[b]

[‡] Percentage errors in our results were calculated based on the corresponding experimental data shown in column 6

[a,b] Experimental data were obtained from [4][a] and [6][b]

was also supported by the study of Royappa et al. [43], who compared 21 potential empirical functions, including the Morse, Deng-Fan. The Rosen-Morse potential functions in fitting experimental data for some first- and second-row diatomic molecules and suggested that the Morse potential was significantly better than Deng-Fan potential in describing diatomic molecular interaction. Their results also powerfully revealed that the Rosen-Morse potential was considerably better than the Morse potential, consistent with our results as shown in Table 3, particularly for HD, D_2, HT, and T_2 molecules. Our results are in agreement with the study of Wang et al. [35], and Royappa et al. [43] strongly suggested that the Morse potential was better than Manning-Rosen (and therefore Deng-Fan and Schiöberg potential) in describing the interaction of some diatomic molecules. This finding was in contrast to the claim that Deng-Fan potential was better than the Morse potential made by Deng and Fan [33]. The Morse potential was better than the Manning-Rosen potential in predicting vibrational levels of electronic ground states of molecular hydrogen isotopes obtained here was interesting since it was in contrast to results obtained by [34] for the Li_2 molecule. Thus, it suggests that a further investigation on the vibrational energies of these two kinds of molecules for different electronic states is of interest.

The results presented in Table 3 showed that the Modified Rosen Morse potential function was also more accurate in obtaining the first vibrational frequency of the HD, D_2, HT, and T_2 molecules. This finding suggested that the modified Rosen Morse potential was more potent than the Morse potential in describing the interaction of diatomics. This conclusion was supported by the study of Tang et al. [44], who solved the Schrödinger equation of some diatomics with some potential functions and found that the Modified Rosen Morse potential was better in fitting with experimental data. It is interesting to note that for the H_2 molecule (the lightest molecule considered here), the Morse potential was somehow better than both Rosen Morse and the Modified Rosen Morse potential, with errors about 0.31%, 0.37%, and 0.39%, respectively. These errors were related to the accuracy of the semi-classical approximation used in this article which was less accurate for lighter molecules.

To further evaluate our results, the first vibrational frequencies for the molecules generated from our calculations were compared with the most accurate ab-initio estimates adapted from [7,13-14,45-46]. The comparison, shown in Table 4, clearly indicates that our calculations, although having slightly higher % error, are reasonably comparable to the results generated from the ab-initio calculations. The fact that the ab-initio calculations resulted in better accuracy since the ab-initio analysis involved the Born-Oppenheimer, adiabatic, non-adiabatic, relativistic, and quantum electrodynamics effects, which are more comprehensive in comparison to our calculation that only affects the Born-Oppenheimer term applied in a semi-classical approach. As can be seen from Table 4, ab-initio calculations in [45] generated the

Table 4. First vibrational frequencies $v_{1\leftarrow 0}$ ($\Delta J=0$) with % errors[ǂ] using the most accurate potential in this study: Rosen-Morse (RM) and Modified-Rosen-Morse (MRM) potential functions are compared with most accurate corresponding values from ab-initio calculations

Molecule	$v_{1\leftarrow 0(\mathrm{RM})}$ in cm^{-1} (% error)	$v_{1\leftarrow 0(\mathrm{MRM})}$ in cm^{-1} (% error)	$v_{1\leftarrow 0(\text{ab-initio})}$ in cm^{-1} (% error)	$v_{1\leftarrow 0}$ in cm^{-1} (exp.)
H_2	4176.583 (0.37)	4177.203 (0.39)	4161.166 (0) [45] 4161.185(0.0005) [46]	4161.166^a
HD	3641.799 (0.27)	3642.273 (0.28)	3632.160 (0.00003) [45] 3632.179 (0.0005) [46] 3632.158 (0.00008) [14]	3632.161^a
HT	3442.456 (0.22)	3442.885 (0.24)	-	3434.812^b
D_2	2997.124 (0.12)	2997.448 (0.13)	2993.617 (0) [45] 2993.636 (0.0006) [46] 2993.615 (0.00007) [13]	2993.617^a
DT	2744.713 (0.05)	2744.986 (0.06)	-	2743.342^b
T_2	2463.682 (0.03)	2463.901 (0.02)	2464.502 (0.00008) [7]	2464.504^b

[ǂ] Percentage errors were calculated based on the corresponding experimental data in column 5

[a b] Experimental data were obtained from [4]^a and [6]^b

exact experimental values for the first vibrational frequency of H_2 and D_2. They were in excellent agreement with experimental ones for HD (with % error of order 10^{-5}).

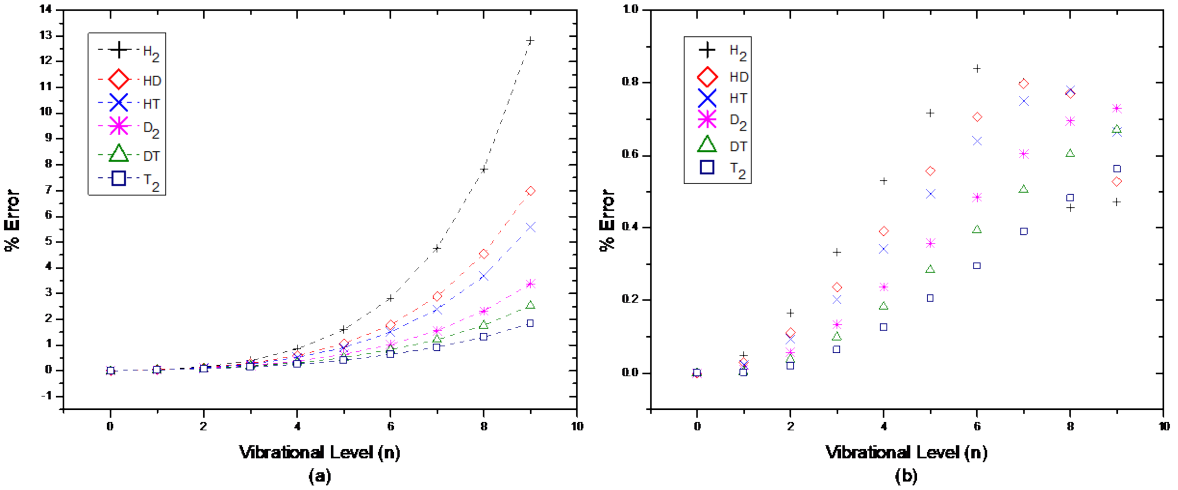
Similarly, the first vibrational frequencies reported in [7,13-14,46] were very accurate with % errors in the order of 10^{-5}–10^{-4} compared to ours with % errors in 10^{-2}–10^{-1}. However, it can be inferred that the Born-Oppenheimer term made the most significant contribution to the vibrational energies of the molecules. The contribution of the Born-Oppenheimer term can reach about 99.9% from the most accurate ab-initio results for the first vibrational frequency $v_{1\leftarrow 0}$ of the molecules [45]. Therefore, despite involving only Born-Oppenheimer approximation in a semi-classical approximation, our products can generate reasonably accurate results with an error below 0.4% for the first vibrational frequencies of the molecules.

Accuracy as a function of the vibrational quantum number and molecular mass

To further clarify the accuracy of the potentials used, the percentage errors provided in Table 2 are plotted against the vibrational levels. The plot for the Morse potential is shown in Fig. 2(a). The pattern for other potentials is similar and hence is not shown.

The results obtained in Fig. 2(a) indicated that at higher vibrational levels, the accuracy of our calculations decreased, as indicated by the increase in the percentage of errors for higher vibrational energies for all molecules considered. This trend was also observed for other isotopes used in this study, as can be seen from Table 2. This finding was interesting since semi-classical approximation should work better for higher energies as for much higher energies, wave functions of the systems should approach the classical free particle wave functions. The more significant errors observed for higher vibrational states in this research were because the values of δ used for a particular molecule using a particular potential were fitted only once for the ground vibrational state energy and used to calculate other higher vibrational energies of the molecules.

Additionally, the use of the Rosen-Morse and the Modified-Rosen-Morse potentials have significantly reduced the errors obtained using the Morse potential, especially for higher vibrational states of the H_2 molecule. This finding can be seen in Fig. 2(b) and Table 2, where the % errors resulted from the use of Rosen-Morse and the Modified-Rosen-Morse potentials were below 1%. These percentage errors were significantly lower than those calculated using the Morse potential,



(a)

(b)

Fig 2. (a) % Errors in our vibrational energies are plotted against the vibrational energy levels for all molecules using the Morse potential and (b) Rosen-Morse potential

with the highest % errors of 12.83%. It was also important to note from Fig. 2(a) that better accuracy was obtained for heavier isotopes. This result was indicated by the more minor errors for heavier isotopes. The argument can explain that the heavier the molecules, the more "classical" they become (the larger γ values they have). This discrepancy was mainly due to the semi-classical approximation is based on the assumption that the nuclei move in classical potential wells. Therefore they have continuous energy like any classical object before their subsequent quantization using the Bohr-Sommerfeld quantization rule.

Consequently, less accurate results generated from this approximation in comparison to the ab-initio calculations would be anticipated. However, better accuracy using this approximation was expected following the substitution of the lighter isotopes with their heavier counterparts within the molecules. As previously described, this change was due to the more classical dynamics of the molecules as the mass of the isotopes increases. This was described as the γ value in Eq. (4). Larger γ values correspond to more 'classical' molecules and more accurate results for the semi-classical approximation. Chemically, this can be attributed to the fact that heavier isotopes have more stable vibrational states than lighter ones, as previously described.

With these two essential observations, investigations of the accuracy of this method on the calculation of vibrational energies of more 'classical' diatomic molecules are therefore attractive. A more comprehensive study on this topic is the subject of our following paper which is in preparation.

Improved Vibrational Energies from the (Modified) Rosen Morse Potential

In our previous study [28], the semi-classical method using the Morse potential has been successfully applied to calculate low-lying vibrational energies of the molecular hydrogen H_2. However, as can be seen from Fig. 2(a), a declining trend in the accuracy was observed for higher vibrational states. This decreasing trend, particularly for higher vibrational states and lighter molecules, was fixed by Rosen-Morse and the Modified-Rosen-Morse potential. This can be seen in Fig. 2(b).

Fig. 2(b) demonstrates that the increase in the errors when using the Morse potential for higher vibrational states of the molecules could be fixed by using the Rosen-Morse potential function. This result was shown by a significant decreasing trend of the % errors for the H_2 molecule, particularly from n = 7 onwards. A similar pattern can also be seen for the HD molecule starting at n = 8. For heavier molecules: HT, D_2, DT, and T_2, the practice is not seen, but a decrease of errors for higher vibrational states (n > 9) is highly expected from the pattern shown in Fig. 2(b). This finding implies that the use of the Rosen-Morse and the

Modified-Rosen-Morse potential function within the framework of the semi-classical approximation has significantly improved the accuracy of the calculation of vibrational energies from the Morse potential, especially for higher vibrational states. This finding was also reported by Tang et al. [44]. They fitted the potentials to the well-known Rydberg-Klein-Rees (RKR) data points of the Li_2 molecule. They found that the modified Rosen Morse potential showed a much better fit with the experimental data than Morse potential, especially for high vibrational states. Zhang et al. [32] also reported the same finding when examining some other diatomic molecules in their study, including ICl, I_2, Cs_2, MgH, and Li_2 molecules. This argument was also valid for other diatomic molecules, including SiC, SCl, Cs_2, and Na_2 molecules, as reported in [47-49]. These observations strongly indicated that the Rosen Morse and the modified Rosen Morse potential were better than the Morse potential (and therefore the Manning-Rosen, Deng-Fan, and the Schiöberg potential) in describing the interaction of some diatomic molecules. More comprehensive studies on other physical and chemical properties of other diatomic molecules in different electronic, vibrational, and rotational states are therefore essential to further evaluate and compare the accuracy of the potential functions in describing the interaction of the molecules.

■ CONCLUSION

The semi-classical method has been successfully applied to obtain the first ten vibrational energies of all isotopes of the molecular hydrogen in their ground electronic state $X\Sigma_g^+$. The results showed that the Rosen-Morse and the Modified Rosen Morse potential were the most accurate potentials used in this study, with errors below 1%. It was also found that the Morse potential was better than the Manning-Rosen potential function in calculating vibrational energy levels of all isotopes of the diatomic hydrogen, using the semi-classical approximation. Finally, the accuracy of the approximation becomes better for heavier isotopes. The semi-classical approximation could be applied to study vibrational energies of diatomic molecules, especially those with larger reduced mass using various classical potential functions.

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