HF, DF, TF: approximating potential curves, calculating rovibrational states

Laura E Angeles-Gantes and Horacio Olivares-Pilón

Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-534, 09340 México, D.F., Mexico

E-mail: horop@xanum.uam.mx

Received 26 October 2021, revised 26 May 2022
Accepted for publication 29 June 2022
Published 18 July 2022

Abstract
A simple analytical expression for the potential energy curve for the ground state $X^1\Sigma^+$ of the hydrogen fluoride molecule HF obtained in the framework of the Born–Oppenheimer approximation is proposed. This analytical expression for the potential energy curve is based in the two point Padé approximation, which correctly reproduces the asymptotic behavior at small $R \to 0$ and large $R \to \infty$ internuclear distances, and position and depth of potential well, leading to the accuracy of 4–5 decimal digits when compared with experimental data. The rovibrational spectra of the diatomic molecule HF is calculated by solving the Schrödinger equation for nuclear motion using the Lagrange-mesh method. The ground state $X^1\Sigma^+$ contains 21 vibrational states $(\nu, 0)$ and 724 rovibrational states $(\nu, L)$ with maximal angular momentum equal to 55. The change of reduced mass in the Schrödinger equation for nuclear motion allows us to obtain the rovibrational spectrum of the ground state potential curve of the deuterium fluoride DF (contains 29 vibrational states $(\nu, 0)$ and 1377 rovibrational states $(\nu, L)$) and tritium fluoride TF (contains 35 vibrational states $(\nu, 0)$ and 1967 rovibrational states $(\nu, L)$) with maximal angular momenta 76 and 92, respectively. Entire rovibrational spectra is presented for the HF molecule and its two isotopologues DF and TF.

Keywords: HF, DF, TF, diatomic molecules, analytic representation, potential energy curve

(Some figures may appear in colour only in the online journal)

1. Introduction

In the analysis of molecular systems within the Born–Oppenheimer approximation, the parametric dependence of the total energy on the nuclear positions defines the potential energy surface (PES). In practice, the PES is given at a set of discrete points in the space of nuclear coordinates which are obtained by solving the electronic motion in the field produced by the fixed nuclei (charged centers).

In the simplest case of diatomic molecules, the PES becomes a potential energy curve (PEC) as a function of the internuclear distance $R$. Nowadays, the development of numerical techniques for quantum-mechanical calculations, has made it possible to obtain highly accurate values of the PEC, however, as is well known, as the number of electrons increases, the accuracy deteriorates while the computational time increases dramatically. An alternative is to extract the PEC from experimental results using the Rydberg–Klein–Rees (RKR) method [1–3], from where the turning points of the vibrational levels are obtained. In order to construct a continuous representation of the PEC, the standard approach consists of fitting the discrete points for PEC by traditional potentials (e.g. Morse, Lennard-Jones, Pöschl–Teller, etc) or to consider more sophisticated expressions for potentials [4] mainly, near equilibrium and sometimes involving the domain of large distances.

In this work we consider the ground state $X^1\Sigma^+$ of the hydrogen fluoride (HF), a diatomic molecule composed of a hydrogen atom $(1e, 1p)$ and a fluorine atom $(9e, 9p)$. This molecule, with 10 electrons in total, has been extensively studied both experimentally and theoretically (see for example [5–10] and references therein). At present, the high accuracy
achieved experimentally has made it possible to obtain very accurate PECs. Theoretically, it has been a challenge to obtain a complete description from \textit{ab initio} calculations. The average absolute deviation between experimental and theoretical vibrational energy levels is $\sim 80$ cm$^{-1}$ ($\sim 4 \times 10^{-4}$ Hartree) [9].

The goal of this paper, is to present an analytical expression for the ground state $\chi^1 \Sigma^+$ of the PEC $V(R)$ in all domain of internuclear distances $R$ with a correct asymptotic behavior at small ($R \to 0$) and large ($R \to \infty$) values of the distance between nuclei. The analytical expression $V(R)$ is given in terms of a two points Padé approximant. The methodology followed here, has been applied successfully to some specific heteronuclear (HeH, LiH and ClF) and homonuclear (H$_2^+$, H$_2$ and He$_2^+$) diatomic molecules [11–13]. The reader is referred to [12], where the method is described in detail.

With the explicit analytical expression of the PEC, the Schrödinger equation for nuclear motion (see below) is solved in Lagrange-mesh method (LMM) to obtain the rovibrational spectra for this diatomic molecule.

Making a simple modification in the nuclear Schrödinger equation—it occurs due to the fact that we make studies in the Born–Oppenheimer approximation—the rovibrational spectra $E_{nLJ}$ is also obtained for the isotopological species with deuterium (D) and tritium (T) content: deuterium fluoride (DF) and tritium fluoride (TF) molecules, respectively.

2. The ground state $\chi^1 \Sigma^+$ of the HF molecule

Let us start by describing the two asymptotic limits, small ($R \to 0$) and large ($R \to \infty$) intermolecular distances of the PEC for the ground state $\chi^1 \Sigma^+$ of the heteronuclear diatomic molecule HF. In the united atom limit ($R \to 0$), we have a neon atom (Ne) and the dissociation energy $\tilde{E}$ for small internuclear distances is given by

$$\tilde{E} = \frac{9}{R} - \varepsilon_0 + O(R^2),$$

(1)

where the first term is the repulsive Coulomb interaction between nuclei and $\varepsilon_0$ is the difference between the energy of the system in the united atom limit (neon atom $E_{Ne}$) and the sum of the energies for each individual components of the molecule, the hydrogen ($E_{HI}$) and fluorine atom ($E_{F}$)

$$\varepsilon_0 = E_{Ne} - (E_{HI} + E_{F}),$$

(2)

with $E_{Ne} = -128.937274$ a.u., $E_{HI} = -0.5$ a.u. and $E_{F} = -99.733424$ a.u. [14]. On the other hand at large intermolecular distances $R \to \infty$, the molecule dissociates into a hydrogen atom plus a fluorine atom, and the dissociation energy is given by

$$\tilde{E} = -\frac{C_6}{R^6} + O\left(\frac{1}{R^8}\right),$$

(3)

where the Van der Waals coefficient $C_6 = 7.766$ a.u. [7] and $C_7 = 0$ a.u. The first term $-1/R^6$ in (3) has the meaning of the interaction potential of two induced dipoles [4] and the other terms in the expansion are related with (hyper)polarizabilities of different orders.

In order to construct an analytic representation for the PEC interpolating the two asymptotic limits $R \to 0$ (1) and $R \to \infty$ (3) a two point Padé type approximant of the form $E(R)_{[n_0,n_\infty]} = \frac{1}{Pade\left[N/N+5\right]}$ is used. This approximation reproduces $n_0$ terms at small and $n_\infty$ terms at large internuclear distances in the energy expansion. Choosing $N = 5$, $n_0 = 3$ and $n_\infty = 2$, the explicit expression for $E(R)_{[3,2]}$ is given by

$$E(R)_{[3,2]} = \frac{9 + a_1 R + a_2 R^2 + a_3 R^3 + a_4 R^4 - C_6 R^6}{R(1 + b_1 R + b_2 R^2 + b_3 R^3 + b_4 R^4 + b_5 R^5 + b_6 R^6 + b_7 R^7 + b_8 R^8 + b_9 R^9 + R^{10})},$$

(4)

In order that the Taylor series of (4) around $R = 0$ correctly reproduces the coefficients of the terms $R^{-1}$, $R^0$ and $R^1$ of the expansion (1), two constraints between some coefficients $a_i$ and $b_j$ must be satisfied

$$b_1 = \frac{a_1 - \varepsilon_0}{9},$$

(5)

$$b_2 = -\frac{a_1 \varepsilon_0 + \varepsilon_0^2 + 9 a_2}{81}.$$  

On the other hand, in order to ensure that the asymptotic series ($R \to \infty$) of (4) correctly reproduces the coefficients of the two terms $R^{-6}$ and $R^{-7}$ of (3), one more constriction appears

$$b_9 = -\frac{a_4}{C_6}.$$  

(6)

The then free parameters have been obtained through a fit of the experimental energy values reported in [8] with the analytic expression (4). Their values result in

$$a_1 = 2761.87, \quad a_2 = -2269.79, \quad a_3 = -193.29, \quad a_4 = 107.967 \quad \text{a}$$

$$b_1 = -660.63, \quad b_4 = 1909.71, \quad b_5 = -1658.58, \quad b_6 = 988.485, \quad b_7 = -379.066, \quad b_8 = 94.677.$$  

(7)
After replacing the values of the parameters (7) and the constraints (5) and (6) in (4), the Taylor series around $R = 0$ of $E(R)_{13,2}$ (4) is given by

$$E(R)_{13,2} = \frac{9}{R} - 28.703850 + O(R^2),$$

(8)

while the asymptotic expansion ($R \rightarrow \infty$) results in

$$E(R)_{13,2} = \frac{7.766}{R^6} + \frac{0}{R^6} + O(R^{-8}),$$

(9)

in complete agreement with (1) and (3), respectively. The values of the parameters (7) are such that all poles of the Padé approximant (4) are negative or complex conjugates.

It is worth mentioning that the results of [8], which we call experimental results, were obtained from an effective Hamiltonian with free parameters which are determined by a least-squares fit to a set of spectroscopic lines from the analysis of the emission band systems between two states [15, 16].

Table 1 presents, in a RRK-style, the turning points $R_{\min}$ and $R_{\max}$ of the PEC and their corresponding energy values $E$ as given in [8], although with different units. The conversion factors used are: 1 Hz $= 0.529177210933$ Å and 1 Hartree $= 2.19474631362 \times 10^6$ cm$^{-1}$ [17] and the dissociation energy $D_e = 49.361$ cm$^{-1}$ [8]. The energy resulting from the evaluation of the analytical expression (4) at the turning points is presented in columns 4 and 5, respectively. As can be seen in table 1, the analytic expression (4) gives no less that 4 significant digits in correspondence with the experimental results [8]. The equilibrium position and the depth of the PEC can be calculated by simply taking the derivative of (4) and setting it equal to zero. As a result, we obtain $R_{eq} = 1.73254$ a.u. and $E_{min} = -0.224913$ a.u. In comparison, the best numerical result is $R_{eq} = 1.73257$ a.u. and $E_{min} = -0.224908$ a.u. [8]. The analytic expression for the PEC (4) as well as the experimental results [8], are depicted in figure 1.

2.1. Rovibrational spectra

In the Born–Oppenheimer approximation, the rovibrational spectrum $E_{\nu,L,j}$ can be obtained by solving the nuclear Schrödinger equation

$$\left( -\frac{1}{2\mu_i} \frac{d^2}{dr^2} + \frac{L(L+1)}{2\mu_i r^2} + V(R) \right) \psi(R) = E_{\nu,L,j} \psi(R),$$

(10)

where $\mu$ is the reduced mass and $\nu$ and $L$ are the vibrational and rotational quantum numbers. For the concrete case of the HF molecule, the interaction potential $V(R)$ is given by the analytic expression (4) and the reduced mass $\mu = m_H m_F / (m_H + m_F)$ is calculated from the nuclear masses of the hydrogen and fluorine atoms: $m_H = 1836.1527$ a.u. and $m_F = 34.622.974$ a.u. [18], respectively.

In order to solve the one dimension differential equation for the nuclear motion (10), the LMM is used [21, 23]. Due to the fact that the domain of the variable $R$ is $[0, \infty)$, in the context of the LMM, a set of $N$ Lagrange functions $f_i(x)$ defined over the same domain is associated with $N$ mesh points $x_i$ which correspond to the zeros of Laguerre polynomials of degree $N$, i.e. $L_N(x_i) = 0$. The Lagrange–Laguerre functions $f_i(x)$ which satisfy the Lagrange conditions

$$f_i(x_j) = \delta_{ij},$$

(11)

at the $N$ mesh points are given by

$$f_i(x) = (-1)^i \frac{N!}{x_i^{i+1/2}} \frac{L_N(x)}{(x - x_i)^{i+1/2}} e^{-x/2}.$$  

(12)

The coefficients $\lambda_i$ are the weights associated with a Gauss quadrature

$$\int_0^\infty G(x)dx \approx \sum_{k=1}^N \lambda_k G(x_k).$$  

(13)

The solution of the Schrödinger equation (10) is expressed by an expansion in terms of the $N$ Lagrange functions $f_i(x)$ (12) as

$$\psi(R) = \sum_{j=1}^N c_j f_j(R).$$  

(14)

The trial function (14), together with the Gauss quadrature (13) and the Lagrange conditions (11) leads to the system of variational equations

$$\sum_{j=1}^N \left[ T_{ij} + \left( \frac{L(L+1)}{2\mu_i x_i^2} + V(x_i) \right) \delta_{ij} \right] c_j = E_{\nu,L,j} c_i,$$

(15)
where $V(x_i)$ is the interaction potential (4) evaluated at the mesh points and $T_{ij}$ are the kinetic-energy matrix elements whose explicit expression is found in [21]. After solving the system (15), it is found that the PEC for the ground state $X^1\Sigma^+$ supports 21 pure vibrational states ($L = 0$) $E_{(\nu,0)}$ with $\nu = 0, \ldots, 20$ in complete agreement with the experimental results presented in [8] (see table 2). The absolute error in the vibrational spectra is $\leq 4 \times 10^{-5}$. For comparison, the experimental data presented in [5] are also shown in table 2. Figure 2 shows the number $N$ of vibrational levels with the same rotational quantum number $L$. It can be noticed that the number of rotational levels $E_{(\nu,L)}$ of the ground state $X^1\Sigma^+$ is 56 ($L = 0, \ldots, 55$). In total the PEC supports 724 rovibrational states. The data from $L = 0, \ldots, 41$ reported in [10] are also depicted in figure 2. The 27 additional states presented in [10] between $L = 9$ and $L = 40$ correspond to quasi-bound states, i.e. states above the dissociation limit.

### Table 2. Vibrational energies $E_{(\nu,0)}$ of the ground state $X^1\Sigma^+$ of the diatomic molecule HF.

| $\nu$ | $E_{(\nu,0)}$ (Hartree) |
|-------|------------------------|
| 0     | -0.215 65              |
| 1     | -0.197 60              |
| 2     | -0.180 33              |
| 3     | -0.163 83              |
| 4     | -0.148 07              |
| 5     | -0.133 04              |
| 6     | -0.118 72              |
| 7     | -0.105 10              |
| 8     | -0.092 18              |
| 9     | -0.079 95              |
| 10    | -0.068 42              |
| 11    | -0.057 60              |
| 12    | -0.047 50              |
| 13    | -0.038 15              |
| 14    | -0.029 60              |
| 15    | -0.021 89              |
| 16    | -0.015 11              |
| 17    | -0.009 36              |
| 18    | -0.004 79              |
| 19    | -0.001 61              |
| 20    | -0.000 10              |

### 3. The ground state $X^1\Sigma^+$ of the DF molecule

The formalism developed previously for the HF molecule allows us to extend the study to the isotopologues DF (deuterium fluorine) and TF (tritium fluorine). Let us start by considering the deuterium-containing molecule DF.

Due to the fact that we are working within of the Born–Oppenheimer approximation, we are not aware of isotopic corrections: the depth of the minimum is the same for all three systems, HF, DF and TF. For this reason, in order to obtain the rovibrational spectrum by solving the Schrödinger
for the nuclear motion (10), the analytic expression for the interaction potential is the same as that for the HF molecule (4). The difference appears in the nuclear reduced mass $\mu = m_T m_F / (m_T + m_F)$ (10), where the deuteron mass is $m_D = 3670.4833$ a.u. [18]. The resulting differential equation was solved using the LMM [21].

Column 4 of table 3, presents the 29 vibrational states $E_{\nu,0,0}$, $\nu = 0, \ldots, 28$ supported by the ground state $X^1\Sigma^+$ of the DF molecule. When comparing with the results obtained from experimental data [10], it is found that the absolute error is $\lesssim 6 \times 10^{-5}$. The origin of this greater deviation with respect to the HF case can be found in the corrections due to isotopic, relativistic, QED, . . . effects which we are not considering. For comparison purposes, column 2 of table 3 display the results given in [22].

The number of vibrational states as a function of the angular momentum number $L$ are depicted in figure 3. There are 77 pure rotational states $E_{0,0,L}$, with $L = 0, \ldots, 76$. In total, the ground state $X^1\Sigma^+$ of the DF molecule supports 1377 rovibrational states. The 87 rovibrational additional states presented in [10] between $L = 14$ and $L = 60$ shown in figure 3, correspond to quasi-bound states.

### Table 3. Vibrational energies $E_{\nu,0,0}$ of the ground state $X^1\Sigma^+$ of the diatomic molecule DF. For comparison, the results presented in [10, 22] are shown in columns 2 and 3, respectively.

| $\nu$ | Reference [22] | Reference [10] | $E_{\nu,0,0}$ |
|-------|----------------|----------------|--------------|
| 0     | -0.21807       | -0.21806       | -0.21812     |
| 1     | -0.20483       | -0.20482       | -0.20487     |
| 2     | -0.19200       | -0.19199       | -0.19204     |
| 3     | -0.17953       | -0.17957       | -0.17962     |
| 4     | -0.16744       | -0.16755       | -0.16760     |
| 5     | -0.15574       | -0.15593       | -0.15597     |
| 6     | -0.14441       | -0.14469       | -0.14473     |
| 7     | -0.13346       | -0.13383       | -0.13387     |
| 8     | -0.12289       | -0.12335       | -0.12339     |
| 9     | -0.11271       | -0.11324       | -0.11328     |
| 10    | -0.10290       | -0.10349       | -0.10353     |
| 11    | -0.09347       | -0.09411       | -0.09415     |
| 12    | -0.08443       | -0.08510       | -0.08513     |
| 13    | -0.07576       | -0.07645       | -0.07648     |
| 14    | -0.06747       | -0.06817       | -0.06819     |
| 15    | -0.05957       | -0.06026       | -0.06028     |
| 16    | -0.05255       | -0.05272       | -0.05275     |
| 17    | -0.04540       | -0.04558       | -0.04560     |
| 18    | -0.03865       | -0.03883       | -0.03885     |
| 19    | -0.03231       | -0.03249       | -0.03251     |
| 20    | -0.02641       | -0.02659       | -0.02661     |
| 21    | -0.02097       | -0.02115       | -0.02117     |
| 22    | -0.01603       | -0.01620       | -0.01621     |
| 23    | -0.01162       | -0.01178       | -0.01179     |
| 24    | -0.00794       | -0.00795       | -0.00795     |
| 25    | -0.00475       | -0.00475       | -0.00475     |
| 26    | -0.00228       | -0.00228       | -0.00228     |
| 27    | -0.00066       | -0.00066       | -0.00066     |
| 28    | -0.00006       | -0.00002       | -0.00002     |

### 4. The ground state $X^1\Sigma^+$ of the TF molecule

Let us now consider the diatomic molecule TF which contains a tritium atom and a fluorine atom. The rovibrational spectra can be calculated in the frame of the LMM [21] by solving the Schrödinger equation for the nuclear motion with Hamiltonian (10) and potential curve (4). For this molecule, $\mu = m_T m_F / (m_T + m_F)$, where the triton mass is $m_T = 5496.9221$ a.u.

As is shown in table 4, in agreement with the experimental results [10], the ground state $X^1\Sigma^+$ of the TF molecule contains 35 pure vibrational states ($L = 0$), $E_{\nu,0,0}$ ($\nu = 0, \ldots, 34$). The absolute error between $E_{\nu,0,0}$ and the experimental results is $\lesssim 8 \times 10^{-5}$. As was the case for the DF molecule, the origin of this greater deviation with respect to the HF case can be found in the corrections due to isotopic, relativistic, QED, etc effects, which we are not considering. It is found that there are 93 rotational states ($\nu = 0$), $E_{\nu,L}$ ($L = 0, \ldots, 92$) and in total the ground state keeps 1967 rovibrational states.

The number $N$ of vibrational levels as a function of the angular momentum $L$ is depicted in histogram of figure 4 together with those reported in [10].
5. Conclusions

Applying the methodology developed in [11, 12], an accurate and simple analytical representation of the PEC for the ground stated $X^1\Sigma^+$ of the hydrogen fluoride (HF) molecule is presented. The approximation is based on a two-point Pade approximant which satisfies the two criteria: (i) it should reproduce correctly the coefficients in the series expansion for small ($R \to 0$) and large ($R \to \infty$) internuclear distances and (ii) two characteristics of the potential well, the equilibrium position $R_{eq}$ and the dissociation energy $E_{\text{min}}$, are reproduced accurately. Finally, the obtained analytical curve is accurate with not less than 4 decimal digits compared with experimental results whenever is possible. It is shown that within the Born–Oppenheimer approximation the PEC keeps 21 vibrational states ($\nu = 0, \ldots, 20, L = 0$), 56 rotational states ($\nu = 0, L = 0 \ldots, 35$) and, in total, 724 rovibrational states ($\nu, L$).

Modification of the reduced mass $\mu$ in the Schrödinger equation for nuclear motion (10) allows us to explore the isotopologues of the HF molecule. It is found that the ground state $X^1\Sigma^+$ of the deuterium fluoride (DF)/tritium fluoride molecule (TF) supports 29/35 vibrational states $E_{\nu,0}$ and 77/93 rotational states $E_{0,L,\nu}$, respectively. The number of vibrational states $E_{\nu,0}$ calculated for the HF, DF and TF molecules is in agreement with those reported in [8, 10]. On the other hand, the maximum value of the angular momentum for rotational states $E_{0,L,\nu}$ is $L_{\text{max}} = 55, 76$ and 92, respectively, (note that in [10] the rovibrational states are presented up to $L = 41, 69$ and 15) for HF, DF and TF diatomic molecules. In the Born–Oppenheimer approximation, the total number of rovibrational states supported by the ground state potential curve are: 724, 1377 and 1967, respectively. For HF and DF, the difference with the results of [10] in the number of vibrational states for a given angular momentum $L$ (figures 2 and 3), when a comparison is possible, is due to taken into account the non-adiabatic terms in the Schrödinger equation for the nuclear motion.

Finally, it is worth mentioning that the same methodology can be applied to study the PECs for both, attractive and repulsive excited states of the HF molecule and its isotopologues DF and TF. Note that with the analytical expressions for the PEC, radiative transitions between different electronic states can be calculated. It will be done elsewhere.

Acknowledgments

The authors thank A Turbiner for bringing the problem to their attention through the work of O Polysansky about the HF dimer, the interest to the work and for the numerous valuable discussions. HOP also thanks the support through the Programa Especial de Apoyo a la Investigación 2019, UAM-I. LAG is grateful to CONACyT (Mexico) for a graduate scholarship.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Horacio Olivares-Pilón https://orcid.org/0000-0002-0353-4337

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