Towards the analytic theory of potential energy curves for diatomic molecules: studying He$_2^+$ and LiH diatomics as illustration

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**ABSTRACT**
Following the first principles, the elements of the analytic theory of potential curves for diatomic molecules (diatomics) are presented. It is based on matching the perturbation theory at small internuclear distances $R$ and multipole expansion at large distances, modified by exponentially small terms for homonuclear case, with the addition of the phenomenologically described equilibrium configuration, if it exists. It leads to a new class of (generalised) rational potentials (modified by exponentially small terms) with a difference in degrees of polynomials in numerator and denominator equal to 4 (6) for positively charged (neutral) diatomics. For example, the He$_2^+$ and LiH diatomics in Born–Oppenheimer approximation are considered. For $^4$He$_2^+$ ($^3$He$_2^+$) diatomics it is found the approximate analytic expression for the potential energy curves (analytic PEC) $V(R)$ for the ground state $X^2\Sigma^+_g$ and the first excited state $A^2\Sigma^+_u$. It provides 3–4 s.d. correctly for distances $R \in [1, 10]$ a.u. with some irregularities for $A^2\Sigma^+_u$ PEC at small distances (much are smaller than equilibrium distances) probably related to level (quasi)-crossings that may occur there. The analytic PEC for the ground state $X^2\Sigma^+_g$ supports 829 (626) rovibrational states with 3–4 s.d. of accuracy in energy, which is only by 1 state less (more) than 830 (625) reported in the literature. The analytic PEC for the excited state $A^2\Sigma^+_u$ supports all 9 reported weakly-bound rovibrational states. For $^7$LiH it is found the analytic expression for the ground state $X^1\Sigma^+$ PEC in the form of a rational function, which supports 906 rovibrational states with 3–4 s.d. accuracy in energy, it is only of 5 states more than reported in the literature (901). For both diatomics, the difference in a number of rovibrational states is related to the non-existence/existence of weakly-bound states close to the threshold (to dissociation limit). Entire rovibrational spectra are found in a single calculation using the code based on the Lagrange mesh method.

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1. Introduction

Developed in molecular physics, the celebrated Born–Oppenheimer (BO) approximation [1] (for discussion, see [2]) takes advantage of the large difference in the masses of the nuclei and electrons. This approach allows to separate the fast (electronic) degrees of freedom from the slow (nuclear) ones. At the first stage in this approximation, the nuclei are assumed to be clamped forming a certain spatial configuration, thus, nuclear masses are infinite and internuclear distances become classical, non-dynamical variables. Hence, the original many-body Coulomb problem becomes the problem of electrons interacting with several fixed Coulomb (charged) centres. Its dynamics is governed by the electronic Hamiltonian,

\[ \mathcal{H}_e = T_e + V(r_e; R_N), \]

where the electronic kinetic energy

\[ T_e = -\frac{1}{2} \sum_i \nabla_i^2 (r_e), \]

is the sum of kinetic energies of individual electrons, where \( \hbar = 1, m_e = 1 \), and the Coulomb potential energy, which is the sum of three terms,

\[ V(r_e; R_N) = V_n(R_N) + V_{en}(r_e; R_N) + V_e(r_e). \]

These terms correspond to internuclear interaction, electron–nuclear interaction and electron–electron interaction, respectively. The coordinates of the nuclei \( \{ R_N \} \) are fixed, becoming classical (non-dynamical), they play a role of the external parameters in the Hamiltonian (1). Due to the translation-invariant nature of the Coulomb potential \( V(r_e; R_N) \), the relative distances between particles appear in the potential only. One can calculate in a straightforward way, usually, numerically, the spectra of the electronic Hamiltonian \( \mathcal{H}_e \), getting the spectra of the electronic energy \( E_e \), in other words, the electronic terms. The obtained electronic energy, or, in other words, the eigenvalue of the electronic Hamiltonian \( \mathcal{H}_e \), depends on the nuclear configuration, thus, leading to the so-called Potential Energy Surface (PES) \( V(R_N) \), where the nuclear configuration occurs as the ‘argument’. It implies that the internuclear distances \( R_{ij} = |R_i - R_j| \) are positive, they are not dynamical variables. In the second stage, the internuclear distances \( R_{ij} \) are restored as dynamical variables and PES \( V(R_N = R_{ij}) \) is taken as the potential for nuclear motion assuming its nuclear mass independence. It is worth noting that in this approach, due to the smallness the mass of electrons \( m_e \) in comparison with the mass of nuclei \( m_N \) the centre-of-mass of the original many-body Coulomb system differs slightly from the centre-of-mass of nuclei. It does not affect PES, but it leads to some small corrections of the order of \( m_e/m_N \) in study of nuclear motion (for discussion, see [3] and references therein). They will be neglected in the present study, since we are focused on the properties of PES.

It must be emphasised that for polyatomic molecules, the PES \( V(R_N) \) can be presented as the sum over 2-, 3- etc. body interactions. Schematically, it can be written as

\[ V(R_N) = V_{2-body}(R_{12}) + V_{3-body}(R_{12}, R_{13}) + V_{2-body}(R_{23}) + \cdots + V_{3-body}(R_{12}, R_{13}, R_{23}) + \ldots . \]

It must be emphasised that 3- and more body interactions are of short range: they die out for large internuclear distances, see [4] and numerous references into there. In the present paper, we will be focussed on diatomic systems \( (N = 2) \) where \( V(R_{N=2}) = V(R_{12}) \), where \( R_{12} \) is the relative distance between the two nuclei (see below), since now on, we denote \( R \equiv R_{12} \).

In the physically important case of diatomic molecules and ions, in particular, of singly-positively-charged diatomic molecular ions of the type \((A + B)^+\) with nuclear charges \( Z_A \) and \( Z_B \) with \((Z_A + Z_B - 1)\) electrons and neutral diatomic molecules \((A + B)\) with \((Z_A + Z_B)\) electrons, on which we will be focused, the nuclear configuration is defined by the single internuclear (classical) distance \( R > 0 \). In this case, the PES becomes the Potential Energy Curve (PEC) \( E_e = V(R) \). From physics point of view, taking charges \( Z_{A,B} \) as probes, the potential

\[ V(R) = \frac{Z_A Z_B}{R} S(R), \]

measures the screening \( S(R) \) of Coulomb interaction of nuclei due to the presence of electronic media, see for illustration Figure 1. Sometimes, the interplay between the Coulomb repulsion at small distances and the Van der Waals attraction at large distances lead to a sufficiently deep minimum in \( V(R) \) at distances of the order of 1 a.u. (other than Van der Waals minimum which is always present and situated usually at large internuclear distances of the order of 10 a.u.) manifesting the existence of the bound states and, finally, the molecule. In the rotation frame, the potential \( V(R) \) is accompanied by a centrifugal term. These states are called the rovibrational states.

Since early days of quantum mechanics, the potential curves attracted a lot of attention while the main emphasis was given to the creation of the models which describe that the vicinity of the potential well is in a maximally accurate manner: the harmonic and Morse oscillators, Pöschl–Teller, Lennard–Jones and Buckingham potentials, and their numerous modifications, see e.g. [5] and references therein and into as well as a recent review [6]. Usually, these models were pure phenomenological;
they never pretend to describe the whole potential curve and total rovibrational spectra other than several lowest quantum states situated close to a minimum of the PEC and the so-called anharmonicity constants. However, since long ago, the present authors considered as the challenge to find a function, which would describe the \textit{ab initio} calculations carried out by Kolos and Wolniewicz [7] for the PEC of the hydrogen molecule H$_2$ as well as experimental data adequately.

A new development happened in [8] where for the first time for three simple molecules H$^+_2$, H$_2$, (HeH) a certain (generalised) meromorphic (rational) potentials of a new type were proposed, which admitted to find the whole rovibrational spectra for a set of electronic terms (PEC) and even some transition amplitudes between different electronic terms [9]. Those potentials were characterised by the correct asymptotic behaviour at small and large internuclear distances. In concrete, the potentials had a form of (generalised) rational functions modified by exponential terms multiplied by other rational functions for the case of homonuclear diatomic molecules.

The goal of this paper is to develop systematically a theory and construct simple analytic potentials modelling PEC, which are able to describe the rovibrational spectra of diatomics. Note that these potentials result from the interpolation between small and large distance behaviour of PEC. In general, they do not assume \textit{a priori} the existence of the global minimum at $R \sim 1$ a.u.: it occurs naturally due to concrete, physics-inspired coefficients in perturbation theory and multipole expansion. The the minimum can be tuned phenomenologically to describe the experimental data. As an illustration of the general construction, two diatomic molecules He$^+_2$ and $^6$LiH will be considered. Since now on in order to simplify notations, sometimes we will address to diatomic molecules and diatomic ions as \textit{diatomics}.

Atomic units are used throughout the paper, although the energy is given in Rydbergs.

**2. Generalities**

Making an analysis of the electronic Hamiltonian for $(A + B)^+$ ion one can find that the potential $V(R)$ at small $R$ is defined via perturbation theory in $R$,

$$V(R) = \frac{Z_A Z_B}{R} + E_{u.i.} + E_1 R + O(R^2),$$

where the first (classical) term comes from the Coulomb repulsion of nuclei, the second term $E_{u.i.}$ is defined by the energy of united ion (u.i.) with total nuclear charge $(Z_A + Z_B)$ with $(Z_A + Z_B - 1)$ electrons, see e.g. [2], § 80.3

It was observed that the linear term $\sim R$ is always absent, $E_1 = 0$, at least, for the ground state [8, 10, 11].

At large distance $R$ the behaviour of the potential curve is such that the leading term is defined by the interaction of the neutral atom with charged atomic ion, it is given by Van der Waals attraction potential with higher corrections in powers of $1/R$,

$$V(R) = \frac{c_4}{R^4} + \frac{c_5}{R^5} + \frac{c_6}{R^6} + \frac{c_7}{R^7} + \ldots, \quad c_4 > 0,$$

see [12] and for recent (extended) discussion, [13]. Here the parameters $c_{4, \ldots}$ are related with (hyper)polarisabilities of different orders, see [2], § 89. For the case of the ground state $c_5 = 0$ and, hence, the term $\sim 1/R^4$ in (3) is absent [12, 13]. The first term $\sim 1/R^4$ in (3) has a meaning of the charge-induced dipole interaction potential, the term $\sim 1/R^6$ corresponds, basically, to charge-induced quadrupole interaction potential.

For the case of neutral diatomics $(A + B)$ (in fact, we consider the interaction of two neutral atoms at a large internuclear distances) the first two coefficients in (3) are usually absent, $c_4 = c_5 = 0$, and we arrive at the expansion

$$V(R) = -\frac{d_6}{R^6} + \frac{d_7}{R^7} + \frac{d_8}{R^8} + \ldots, \quad d_6 > 0.$$  

If the ground state is considered $d_7 = 0$, the first term $\sim 1/R^6$ in (4) has a meaning of the interaction potential of two induced dipoles, the term $\sim 1/R^8$ corresponds to induced dipole-induced quadrupole interaction potential etc., see e.g. [14] for the case of hydrogen molecule H$_2$.
It is evident that the attraction at large distances together with repulsion at small distances implies the existence of the minimum in the potential curve for both diatomic molecular ion and molecule. This minimum occurs at the moment when repulsion is changed to attraction. If this minimum is situated at large distances and (very) shallow, such a minimum is usually called the Van der Waals minimum. It is worth noting that for the case of the molecular ion \((A + B)^+\) the expansion (3) remains the same functionally for both dissociation channels: \(A^+ + B\) and \(A + B^+\), while evidently, the expansion (2) at small distances remains the same for those channels, naturally, it does not see any difference between channels.

In many cases, the known potential curves are smooth curves with slight irregularities, probably, due to effects of the level (quasi)-crossing with other excited states of the same symmetry, see for discussion e.g. [2, 12]. It hints to interpolate the expansions (2)–(3) using a two-point Padé approximation

\[ V_{\text{ion}}(R) = \frac{Z_A Z_B}{R} \frac{P_N(R)}{Q_{N+3}(R)} = \frac{Z_A Z_B}{R} \text{Pade}(N/N + 3), \tag{5} \]

where \(P_N, Q_{N+3}\) are polynomials in \(R\) of degrees \(N, (N + 3)\), respectively, with normalisation \(P_N(0) = Q_{N+3}(0) = 1\), as it was introduced for the first time in [8] for \(H^+_2\) molecular ion, with condition \(Q_{N+3} > 0\) for \(R > 0\). The condition of positivity of denominator \(Q_{N+3}(R)\) in (5) (implying the absence of real positive roots) leads to constraints on its coefficients, not for any \(N\) this condition can be fulfilled. This formula seems applicable for \(any\) singly-positively-charged diatomic molecular ion, for both hetero- and homo-nuclear diatomics. Similar formula can be constructed for the case of neutral diatomics \((A + B)\) with dissociation channel \(A + B\) as interpolation of the expansions (2)–(4),

\[ V_{\text{neutral}}(R) = \frac{Z_A Z_B}{R} \frac{P_N(R)}{Q_{N+5}(R)} = \frac{Z_A Z_B}{R} \text{Pade}(N/N + 5), \tag{6} \]

where \(P_N, Q_{N+5}\) are polynomials in \(R\) of degrees \(N, (N + 5)\), respectively, with normalisation \(P_N(0) = Q_{N+5}(0) = 1\) as it was introduced in [8] for \(H_2\) molecule with condition \(Q_{N+5} > 0\) for \(R > 0\). The condition of positivity of denominator \(Q_{N+5}(R)\) in (6) implies the absence of real positive roots, it leads to constraints on its coefficients, also not for any integer \(N\) it can be fulfilled in practice.

Parameter \(N\) in (5) and (6) takes integer values, \(N = 0, 1, \ldots\). Polynomials \(P_N, Q_{N+k}\) are chosen in such a way that some free parameters in \(\text{Pade}(N/N + k)\) for \(k = 3, 5\) are fixed in order to reproduce exactly several leading coefficients in the both expansions (2)–(3). The remaining free parameters are found to reproduce the potential at some points in \(R\) where the potential is known numerically from solving the electronic Schrödinger equation (the so-called \textit{ab initio} calculations) or experimentally. It might be considered as the surprising fact that the leading coefficients in the expansions (2)–(4) at \(R = 0, \infty\) ‘\textit{know’} about the existence/non-existence of the global, non-Van der Waals minimum at \(R = R_{eq}\). It is worth mentioning if such a minimum exists at \(R = R_{eq}\) remaining free parameters in (5) and (6) can also be found by expanding \(V_{\text{ion}}(R), V_{\text{neutral}}(R)\) near minimum making the Taylor expansion around

\[ V(R) = -D_e + \sum_n f_n (R - R_{eq})^n, \]

where \(D_e\) is the dissociation energy, \(R_{eq}\) is the equilibrium distance (it corresponds to the position of the minimum) and \(f_n\) are the molecular or (an)harmonic constants, or, in the Dunham expansion

\[ V(R) = D_e \left[ \left( 1 - e^{-\alpha(R-R_{eq})} \right)^2 + P_3 \left( 1 - e^{-\alpha(R-R_{eq})} \right)^3 \right. \]
\[ \left. + P_4 \left( 1 - e^{-\alpha(R-R_{eq})} \right)^4 + \ldots \right], \]

where \(\alpha\) is the Morse constant, \(P_3, \ldots\) are parameters, see [15]. Important characteristic of the PEC is \(R = R_0\), where

\[ \tag{7} \]

and the dissociation energy vanishes. Usually, at \(R_0 < R_{eq}\), the potential is positive. For \(R > R_0\), the potential gets negative, the bound states (if they exist) are localised inside this domain. Influence of the behaviour of the potential curve at \(R < R_0\) on the bound states positions needs to be investigated.

In the case of identical nuclei \(A = B\) (homonuclear case) the system \((A + A)^+\) is permutationally-invariant \(Z_A \leftrightarrow Z_B\) and the extra quantum number – parity with respect to the interchange of the nuclei positions, situated symmetrically on the molecular axis at \(0, 0, -\frac{R_{eq}}{2}\) and \((0, 0, \frac{R_{eq}}{2})\) – occurs. This charge exchange energy (or, saying differently, the energy gap) – the difference between two potential curves \(\Delta E = (E_+ - E_-)\) of the first \((k + 1)\)th excited state (of the negative parity) \(E_-\) and of the ground \((k\)th excited) state (of the positive parity) \(E_+\) tends to zero exponentially at large \(R\),

\[ \Delta E = D_0 e^{-\frac{S_0}{R}} \left( 1 + \frac{e^R}{R} + \ldots \right), \]

where \(D_0 > 0\) is monomial in \(R\). Furthermore, as the general feature, the exponent \(S_0 = \alpha R\) always, where the parameter \(\alpha\) depends on the diatomics explored [16], see
below. It implies that these potential curves can be written at large $R$ in the following form,

$$E_\pm = E_0(R) \pm \frac{1}{2} \delta_\pm E(R),$$

(8)

where $E_0(R)$ is given by multipole expansion (3), it is the same for the lowest energy states of both parities, hence, it does not depend on the state. It is clear that both $\delta_\pm E$ are exponentially small. A similar phenomenon of the pairing of the states of opposite parities at large $R$ occur for the potential curves of the $(k+1)$th and $4k$th excited states.

In the profoundly studied case of $H_2^+$ molecular ion, carried out in the remarkable paper [17], the expansion of $\delta_\pm E$ looks like the so-called trans-series: it is the expansion in exponentially-small terms (multi-instanton contributions), each of them accompanied by perturbation theory series in $1/R$ of a special structure; it is similar to the expansion for one-dimensional quartic double-well potential,

$$\delta E_\pm = D_0 e^{-S_0} \left( 1 + \frac{e}{R} + O\left(\frac{1}{R^2}\right) \right)$$

$$\pm D_1 e^{-2S_0} \left( 1 + \frac{e_1}{R} + O\left(\frac{1}{R^2}\right) + a \log R \right) + \ldots,$$

(9)

c.f. [18, 19] (and references therein), where $e, e_1, a$ are constants, $D_0 = \frac{1}{2} R$, $D_1 \sim R^3$. The energy gap has the form

$$\Delta E(R) \equiv \frac{\delta E_- + \delta E_+}{2} = D_0 e^{-S_0}$$

$$\times \left( 1 + \frac{e_1}{R} + O\left(\frac{1}{R^2}\right) \right) + \ldots,$$

(10)

where exponent $S_0 = R$ looks as the classical action (one-instanton contribution): tunnelling between two identical Coulomb wells, situated at $R = \infty$; $D_0 = \frac{1}{2} R$ looks like the one-instanton determinant in semi-classical tunnelling between two identical Coulomb wells.

In all concrete cases, the present authors are familiar with ($H_2^+$, $H_2$, $He_e^+$, $Li_e^+$, $Be_e^+$) diatomic molecular systems the exponent $S_0$ is linear in $R$ (according to [16]) with coefficients that depend on the system studied, $S_0 = \alpha R$, see [8, 20] and references therein (see Table 1). In turn, the factor $D_0$ in (10) is such that $D_0 \sim R$ for $H_2^+$, $D_0 \sim R^{1/2}$ for $He_e^+$ (see below), $D_0 \sim R^{5/2}$ for $H_2$, see e.g. [8], while in all other cases, where it is known, $D_0 \sim R^0$, hence, it is monomial in $R$ of some degree $\beta$. It is worth emphasising that the exponential smallness at large $R$ of the energy gap implies the well-known fact that the multipole expansions (3) for the ground state and the first excited state coincide. In turn, at small $R$, the expansion

| $H_2^+$ | $H_2$ | $He_e^+$ | $Li_e^+$ | $Be_e^+$ |
|---------|---------|-----------|-----------|-----------|
| $\alpha$ | 1       | 2         | 1.344     | 0.629     | 0.829     |
| $\beta$  | 1       | 5/2       | 1/2       | 2.1796    | 1.4125    |

of the energy gap in $R$ is given by the Taylor series

$$\Delta E(R) = \delta_\alpha + \delta_\beta R + O(R^2).$$

(11)

where $\delta_\alpha = E_+^{u,a} - E_+^{a,u}$ is the difference between the first excited state and the ground state energies of the united atom (u.a.) in the case of neutral molecule, or $\delta_\alpha = E_{+1}^{+1} - E_{+1}^{-1}$ is the difference between the first excited state and the ground state energies of the united ion in the case of positively-charged molecular ion.

The next step is to construct an analytic approximation of the exchange energy $\Delta E$ which interpolates the small (11) and large (10) internuclear distances. If $D_0 \sim R^n$ in (10), where $n$ is an integer, this is realised using two-point Padé type approximation

$$\Delta E(R)_{\{n_0,n_\infty\}} = e^{-S_0} P_{N+n}(R) |_{\{n_0,n_\infty\}}$$

$$\equiv e^{-S_0} \text{Pade}\left[\frac{N+n}{N}\right]_{\{n_0,n_\infty\}}(R),$$

(12)

where $P_{N+n}(R)$ and $Q_N(R)$ are polynomials of degrees $N+n$ and $N$, respectively. This approximation supposes to reproduce exactly the first $n_0$ terms at small internuclear distances and the first $n_\infty$ terms at large internuclear distances expansion, respectively. If degree $n$ in $D_0 \sim R^n$ in (10) is half-integer, the formula (12) should be modified, the change of variable is needed: $r = \sqrt{R}$. In particular, for $n = 5/2$ and $S_0 = 2R$ (it is the case of $H_2$ molecule), the two-point Padé type approximation has the form

$$\Delta E(R = r^2)_{\{n_0,n_\infty\}} = e^{-2r^2} P_{N+5}(r) |_{\{n_0,n_\infty\}}$$

$$\equiv e^{-S_0} \text{Pade}\left[\frac{N+5}{N}\right]_{\{n_0,n_\infty\}}(r),$$

(13)

see [8]. In order to reproduce properly the behaviour of the first $n_0$ terms at small internuclear distances (11) and the first $n_\infty$ terms at large (10) internuclear distances the evident constraints on the parameters of the polynomials $P_{N+n}(r)$ and $Q_N(r)$ are imposed. If the degree $n$ in $D_0 \sim R^n$ is some real number, see Table 1, a modification of (12) (or (13)) implies that the regularisation of the
determinant (see a discussion above) is needed,
\[ D_0(R) \rightarrow D_0(R + A), \quad A > 0, \]
where \( A \) is found via fitting the experimental data for the potential curves. It will be done elsewhere.

Due to the exponentially small in \( R \) dependence of \( \delta E_\pm (8) \), the main contribution to the potential curves \( E_\pm \) at large internuclear distances comes from the mean energy \( E_0(R) \),
\[ E_0(R) = \frac{E_+ + E_-}{2}, \tag{14} \]
see (8). Neglecting two-instanton contribution (~ \( e^{-2S_0} \)) and other higher order exponentially-small contributions, the mean energy \( E_0(R) \) expansion at large distances is given by (3). On the other hand, at small internuclear distances \( E_0(R) \) expansion has the same structure as (2) with \( Z_A = Z_B \equiv Z \), where
\[ E_{u.a.} = \frac{E_{+}^{u.a} + E_{-}^{u.a.}}{2}, \]
is the mean energy of the ground and first excited state of the system in the united atom (u.a.) limit, respectively. The analytic approximation for mean energy \( E_0 \) which mimics the asymptotic expansions for small (2) and large (3) distances is again two-point Padé approximation of the form (5)
\[ E_0(R)_{\{n_0, n_\infty\}} = \frac{Z^2}{R} \left( \frac{P_N(R)}{Q_{N+3}(R)} \right)_{\{n_0, n_\infty\}} \equiv \frac{1}{R} \text{Pade}[N/N + 3](n_0, n_\infty)(R). \tag{15} \]
This approximation supposes to reproduce the first \( n_0 \) terms at small and the first \( n_\infty \) terms at large intermolecular distances expansion for mean energy \( E_{u.a.} \).

This procedure has already been applied successfully to the diatomic molecular hydrogen ion \( H_2^+ \) \((p, p, e) \) [8]. In order to illustrate further an approach to the general theory of the potential curves presented above the diatomic molecular ion \( \text{He}_2^+ \) \((\alpha, \alpha, 3e) \) will be considered as an example. Our concrete goal is to construct simple analytic expressions for the PEC of the ground state \( X^2\Sigma^+_u \) and the first excited state \( A^2\Sigma^+_g \) in full range of intermolecular distances.

3. Molecular ion \( \text{He}_2^+ \) as the example

3.1. Introduction

Theoretical studies of \( \text{He}_2^+ \) have been carried out for many years since the pioneering work by L. Pauling [22]. Already in that paper, it was found out explicitly that the ground state PEC exhibits a well-pronounced minimum indicating the existence of the molecular ion \( \text{He}_2^+ \). This observation by Pauling was confirmed later in subsequent theoretical studies (see e.g. [23, 24] and references therein). However, despite the fast development of numerical methods and computer power, an accurate description of the potential energy curves for the \( \text{He}_2^+ \) is still running. Only recently, the PEC for the ground state was presented with absolute accuracy of 0.05 cm\(^{-1}\) in domain \( R \in [0.9, 100.] \) a.u. in the form of a mesh of the size 0.1 a.u. for small and 1 a.u. for large internuclear distances, minimum of the potential well was localised at \( R_{eq} = 2.042 \) a.u. [25]. The same time the present authors are unaware of studies for \( R < 0.9 \) a.u. It was found the ground state electronic term for \( R > 9 \) a.u. is very smooth curve without any irregularities. The above-mentioned accuracy but for excited states has not been yet achieved to the best of the present author’s knowledge. Note that for the first excited state \( A^2\Sigma^+_g \) it was found some irregularity in PEC at distances smaller than equilibrium one, \( R < R_{eq} \) (see [23] and references therein), probably, due to level quasi-crossing(s) with higher excited states of the same symmetry, meanwhile the Van der Waals minimum occurs at large distances \( R_{eq} \sim 9 \) a.u. The influence of that irregularity of the potential curve on rovibrational spectra needs to be investigated. Finally, the knowledge of accurate analytic expressions for the PEC allows us to calculate easily the rotational and vibrational states by solving the Schrödinger equation for the nuclear motion with analytic potential.

3.2. The energy gap \( \Delta E \)

Let us start considering the behaviour of the energy gap \( \Delta E \) between the excited state \( A^2\Sigma^+_g \) and the ground state \( X^2\Sigma^+_u \),
\[ \Delta E = E_{A^2\Sigma^+_g} - E_{X^2\Sigma^+_u}. \]
Following Bingel [10] and also [39] for small internuclear distances \( R \rightarrow 0 \), the behaviour is given by
\[ \Delta E = \delta_0 + 0 \cdot R + O(R^2), \tag{16} \]
where
\[ \delta_0 = E^{Be^+}_2{^2S}_{1/2} - E^{Be^+}_2{^2P}_{1/2}, \]
is the difference between the (rounded) energies of the Beryllium ion \( Be^+ \) [26],
\[ E^{Be^+}_2{^2S}_{1/2} = -28.649 526 \text{ Ry}, \]
\[ E^{Be^+}_2{^2P}_{1/2} = -28.358 666 \text{ Ry}. \tag{17} \]
As for large internuclear distances $R \to \infty$, the energy gap $\Delta E$ is given by [20, 21]
\[
\Delta E = R^{1/2} e^{-\alpha_0 R} \left[ \epsilon_0 + \frac{\epsilon_1}{R} + \frac{\epsilon_2}{R^2} + \cdots \right],
\]
where $\alpha_0 = 1.344$, $\epsilon_0 = 6.608573$, $\epsilon_1 = 2.296763$ and $\epsilon_2 = 0.252798$. Now, we look for an expression that interpolates the expansions (16) and (18). In order to do that, a new variable is introduced
\[
r = \sqrt{R},
\]
and at the same time the parameters $\epsilon_1$ and $\epsilon_2$ are released, which gives more flexibility to the approximation. The two-point Padé-type approximation is given by
\[
e^{-1.344 r^2} \text{Pade}[N + 1/N](r).
\]
Explicitly, taking $N = 11$,
\[
\Delta E_{[2,1]} = e^{-\alpha_0 r^2} \frac{\delta_0 + \alpha_0 \delta_0 r^2 + \sum_{i=2}^{5} a_i r^{2i} + \epsilon_0 r^{12}}{1 + b_1 r^7 + b_2 r^9 + r^{11}}.
\]
After making fit with the numerical results of [24] the six free parameters take values
\[
a_2 = -123.748, \quad b_1 = -1.15654, \\
b_2 = 214.186, \quad b_2 = 4.04014, \\
a_4 = -108.275, \\
a_5 = 46.8906.
\]
The asymptotic behaviour of the expression for $\Delta E_{[2,1]}$ (20) reproduces exactly the first two terms for small internuclear distances $R \to 0$ (16), $n_0 = 2$, and one term for large internuclear distances $R \to \infty$ (18), $n_\infty = 1$.
Comparison between the fit (20) and the numerical results [24] is presented in Figure 2.

### 3.3. The mean energy $E_0$

The dissociation energy for the ground $X^2\Sigma_u^+$ and the first excited state $A^2\Sigma_g^+$ at small internuclear distances $R \to 0$ is given by
\[
\begin{align*}
\bar{E}^{(0)}_{X^2\Sigma_u^+} &= \frac{2Z^2}{R} + (E_{\text{Be}^+}^{\text{Be}^+} + |E_{\infty}|) + 0 \cdot R + O(R^2), \\
\bar{E}^{(0)}_{A^2\Sigma_g^+} &= \frac{2Z^2}{R} + (E_{\text{Be}^+}^{\text{Be}^+} + |E_{\infty}|) + 0 \cdot R + O(R^2),
\end{align*}
\]
where $Z = 2$, $E_{\text{Be}^+}^{\text{Be}^+}$ and $E_{\text{Be}^+}^{\text{Be}^+}$ are given by (17) and
\[
E_{\infty} = E_{\text{He}} + E_{\text{He}}^+ = -1.382874 + 0.807449 + 4.000000,
\]
is the asymptotic energy of the diatomic molecule $\text{He}_2^+$. The asymptotic behaviour of the expression for $\bar{E}^{(0)}$ (21) is given by
\[
\frac{1}{R} \text{Pade}[N/N + 3]_{[3,3]}(R),
\]
where it is required that the first three terms of the expansions at both small and large distances should be reproduced exactly. Explicitly, by choosing the approximant at

![Figure 2](image-url)
$N = 6$ we get

$$E_{0(3,3)} = \frac{8 + \sum_{i=1}^{5} a_i R^i - C_4 R^6}{R(1 + \alpha_1 R + \alpha_2 R^2 + \sum_{i=3}^{6} b_i R^i - \alpha_7 R^7 - \alpha_6 R^8 + R^9)},$$

(26)

with four constraints between parameters

$$\begin{align*}
\alpha_1 &= (a_1 - C_0)/8, \\
\alpha_2 &= (8a_2 - a_1 C_0 + C_0^2)/64, \\
\alpha_7 &= (C_6 + a_4)/C_4, \\
\alpha_8 &= a_5/C_4.
\end{align*}$$

(27)

These constraints guarantee the first three terms in each expansion (23) and (25) are reproduced exactly when (26) is expanded at small and large $R$. The remaining nine parameters in (26) are fixed fitting the all numerical results obtained in [24]

$$\begin{align*}
a_1 &= 471.867, \quad b_3 = 103.213, \\
a_2 &= -706.524, \quad b_4 = -515.786, \\
a_3 &= 474.091, \quad b_5 = 623.091, \\
a_4 &= -148.695, \quad b_6 = -350.333, \\
a_5 &= 21.8549.
\end{align*}$$

Comparison of the fit (26) and the numerical results [24] is made in Figure 2.

### 3.4. Potential energy curves

Explicit analytic expressions for mean energy $E_0$ (26) and energy gap $\Delta E$ (20) allow us to recover the potential energy curves for the ground $X^2 \Sigma_u^+$ and first excited $A^2 \Sigma_g^+$ states,

$$E_{X^2 \Sigma_u^+/A^2 \Sigma_g^+} = E_0 \mp \frac{1}{2} \Delta E.$$

(28)

As a result it reproduces with accuracy 3–4 s.d. the total energy for the ground state and for the first excited state in the entire domain in $R > 0$ when compared with results [24], it is shown in Table 2, with the exception of the domain $0.5 \leq R \leq 1.5$ a.u. for the first excited state A2 $\Sigma_g^+$, where the deviation is significant.

The minimum of the ground state $X^2 \Sigma_u^+$ electronic term is calculated by vanishing the first derivative of the expression (28) gives $E_I = -0.18164$ Ry at $R_{eq} = 2.041$ a.u. For comparison, the $ab\;initio$ calculations carried out in [24] give $E_I = -0.18176$ Ry at $R_{eq} = 2.043$ a.u., while the most accurate numerical result at present leads to $E_I = -0.18184$ Ry at $R_{eq} = 2.042$ a.u. [25]. The crossing of the potential curve (28) with the horizontal line $E = 0$ occurs at $R_0 = 1.4083$ a.u. in agreement with [24], where it should be inside the domain $1.4 < R < 1.5$ a.u.

The Van der Waals minimum for the state $A^2 \Sigma_g^+$ is located at $R = 8.741$ a.u. with depth $E_I = -0.000158$ Ry [24], while (28) predicts $R = 8.362$ a.u. with $E_I = -0.000198$ Ry. Note that the fit (28) predicts the crossing point $R_0 = 7.1066$ a.u. in agreement with the results by Xie et al. [24]: $6.7 < R < 7.4$ a.u.

As it is seen in Table 2 even though the simple analytic approximation (28) predicts reasonably correct the position and the depth of the minima for both states, comparison with results by [23] reveals at $R < 1.5$ a.u. a significant deviation for the excited state $A^2 \Sigma_g^+$ as well as a small insignificant deviation for the ground state $X^2 \Sigma_u^+$, see [25]. For the state $A^2 \Sigma_g^+$ the PEC displays irregularity at $0.5 \leq R \leq 1.5$ a.u. which can be attributed to a quasi-crossing with the next $\Sigma_g$ excited state. Interestingly, the

| $R$ | $X^2 \Sigma_u^+$ | $A^2 \Sigma_g^+$ | $R$ | $X^2 \Sigma_u^+$ | $A^2 \Sigma_g^+$ |
|-----|-----------------|-----------------|-----|-----------------|-----------------|
| 1.0 | 0.78489         | 2.72578         | 2.65| -0.13865        | 0.21102         |
| 0.66628 | 1.59046         | -0.13846        | 0.66537 |
| 0.44602 | 0.13358         | 0.14549         | 0.42043 |
| 0.23859 | 0.66425         | 0.06189         | 0.6236 |
| 0.10222 | 0.03416         | 0.02682         | 0.13654 |
| 0.010544 | 0.03420         | 0.027232        | 0.47491 |
| 0.001662 | -0.00927        | 0.00462         | 0.000787 |
| 0.000766 | -0.00891        | 0.003852        | 0.47491 |
| 0.006220 | 1.36915         | 0.000319        | 0.00077 |
| 0.006218 | 1.36908         | 0.000296        | 0.00072 |
| 0.006236 | -0.00020        | 0.000148        | 0.00072 |
| 0.014419 | 0.97461         | 0.00174         | 0.00011 |
| 0.014416 | 0.974356        | 0.008016        | 0.00012 |
| 0.01431 | -0.001949       | 0.000159        | 0.00012 |
| 0.016507 | 0.82239         | 0.000025        | 0.00017 |
| 0.016496 | 0.822274        | 0.000024        | 0.000148 |
| 0.016508 | -0.000023       | 0.000160        | 0.000148 |
| 0.017662 | 0.69514         | 0.000909        | 0.000160 |
| 0.017656 | 0.695202        | -0.000108       | 0.000160 |
| 0.017668 | -0.0000106      | 0.0000012       | 0.000160 |
| 0.20 | -0.18126        | 0.58884         | 0.000175 | 0.0000012 |
| -0.18132 | 0.588949        | 0.00000102      | 0.000160 |
| -0.18143 | -0.000160       | 0.00000126      | 0.000160 |
| 0.21 | -0.18092        | 0.49991         | -0.000013 | 0.00000126 |
| -0.18106 | 0.499976        | -0.0000108      | 0.00000126 |
| -0.18115 | -0.0000126      | -0.00000126     | 0.00000126 |
| 0.22 | -0.17703        | 0.42534         | -0.000011 | 0.00000098 |
| -0.17716 | 0.425350        | -0.0000102      | 0.00000098 |
| -0.17723 | -0.0000105      | -0.00000115     | 0.00000098 |
| 0.24 | -0.16260        | 0.30989         | -0.000007 | 0.00000057 |
| -0.16254 | 0.309830        | -0.0000007      | 0.00000057 |
| -0.16260 | -0.0000069      | -0.0000007      | 0.00000057 |

Note: The second and third lines for given $R$ display the results of [24, 25], respectively. For $R = 1.0$ a.u. the second line result is from [23].
pattern of irregularity presented in [23] and in (28) are similar qualitatively, see Figure 3. Note that the irregularity occurs for energies much above the threshold energy \( E(\text{He}) + E(\text{He}^+) \), it should not bring much influence to the rovibrational spectra.

Surprisingly, for \( X^2 \Sigma_u^+ \) state fit (28) also predicts a certain irregularity in the domain of \( 0.9 \leq R \leq 1.5 \) a.u. as it can be seen in Figure 3: Numerical data from [25] deviate from our analytic curve as well as from one obtained in [23] in this domain. Since it is relatively small and is situated far above the threshold energy, we do not expect much influence to the rovibrational spectra. Subsequent calculations confirm this prediction, see below.

It can be checked that the asymptotic expansion of fit (28) for the ground state \( X^2 \Sigma_u^+ \) at \( R \to 0 \) is given by

\[
E_{X^2 \Sigma_u^+} = \frac{8}{R} - 18.842078 + 0 \cdot R + \ldots
\]

while the expansion at \( R \to \infty \) has the form

\[
E_{X^2 \Sigma_u^+} = -\frac{1.382874}{R^4} - \frac{3.193540}{R^6} + \ldots - e^{-1.344 R} R^{1/2} \times \left[ 3.304287 + \frac{10.09552}{R} + \ldots \right].
\]

As for the excited state \( A^2 \Sigma_g^+ \) the asymptotic behaviour of (28) are

\[
E_{A^2 \Sigma_g^+} = \frac{8}{R} - 18.551218 + 0 \cdot R + \ldots
\]

\[
E_{A^2 \Sigma_g^+} = -\frac{1.382874}{R^4} - \frac{3.193540}{R^6} + \ldots + e^{-1.344 R} R^{1/2} \left[ 3.304287 + \frac{10.09552}{R} + \ldots \right].
\]

For both states, these expansions are in agreement with the asymptotic behaviour (cf. (21) and (24)).

### 3.5. Rovibrational states

In the Born–Oppenheimer approximation, the rovibrational states are calculated by solving the one-dimensional radial Schrödinger equation for the nuclear motion

\[
\left[ -\frac{1}{\mu} \frac{d^2}{dR^2} + \frac{L(L+1)}{\mu R^2} + V(R) \right] \phi(R) = E_{\nu L} \phi(R),
\]

where \( \mu = M_\alpha/2 = 3647.149771 \ldots \), is the reduced mass of two \( \alpha \) particles, here \( \nu \) and \( L \) are the vibrational and rotational quantum numbers, respectively: any state will be marked as \( (\nu, L) \). It implies that we study the rovibrational state of the diatomic \( ^4\text{He}_2^+ \).

Usually, Equation (32) is solved numerically with the potential \( V(R) \) defined at a discrete set of points in \( R \) as the result of the ab initio calculations. In our case, the potential \( V(R) \) is given by some analytic expression for the potential energy curve (28) (emerging from the expressions (20) and (26)). In this case, the Lagrange-mesh method [27] can be used in its generality in a very efficient and economic way.

It can be immediately obtained using the Lagrange-mesh method that the PEC for the ground state \( X^2 \Sigma_u^+ \) (28) supports 24 vibrational states \( (\nu, 0) \) and 59 rotational states \( (0, L) \), thus, with \( L_{\text{max}} = 58 \). In total, we found 829 rovibrational states \( (\nu, L) \), one state less than the 830 states reported previously in [25]. It is worth mentioning that the rovibrational state energies in [25] were obtained with including adiabatic corrections into the PEC. All found states are presented in a histogram in Figure 4. Making a careful comparison of our results with those in [25] one can see that they agree in 3–4 s.d.

In BO approximation, the PEC for \( ^3\text{He}_2^+ \) and \( ^4\text{He}_2^+ \) coincide by construction, however, small adiabatic corrections make these curves different, usually, in the 4th s.d., see for discussion [25]. It is natural to assume that rovibrational energies are changed by adiabatic corrections in 3–4 s.d., which is consistent with the accuracy of analytic approximations of the PEC we use in the present work. With the analytic expression for the PEC (28) in BO approximation, by making a simple replacement of the nuclear mass of \( ^4\text{He} \) (\( \alpha \) particle) by the nuclear mass of \( ^3\text{He} \) (in the reduced mass) in the radial Schrödinger Equation (32), the rovibrational spectra for diatomics \( ^3\text{He}_2^+ \) can be recalculated. Considering

\[ m_{^3\text{He}} = 5495.88512 \text{ a.u.,} \]
dots, is also reported in [25], where adiabatic corrections are included, unlike in the present paper.

The additional weakly-bound state, presented by space filled by dots, is also reported in [25], where adiabatic corrections are included, unlike in the present paper.

To find that the ground state keeps 21 vibrational states $E_{v=0}$ with $\nu = 0, \ldots, 20$ in agreement with [25] in 3–4 s.d., while the maximum angular momentum is $L_{\text{max}} = 50$. In total, the state $X^2 \Sigma^+_u$ supports 626 rovibrational states, one state more than the 625 states reported in [25]. Note that with a decrease in the reduced mass of the two-body system, both the number of (ro)vibrational states and maximal angular momentum get smaller.

Applying the same procedure for the PEC of the first excited state $A^2 \Sigma^+_g$, our results point out the presence of nine rovibrational states, the same number of states as was found in [24] (see Table 3). In general, the obtained rovibrational energies are very small, being of the order $10^{-5} - 10^{-6}$ Ry (or even less), while one can speculate that adiabatic corrections (as well as relativistic and QED corrections) are of the order $1/\mu \sim 10^{-4}$ as well as the accuracy with PEC was obtained. Even though all our results are stable inside of the Lagrange-mesh method, they fall well beyond our precision. It is worth mentioning that we predict the rotational state $(0,5)$, which is not found in [24], while in [24] it is predicted the vibrational state $(2,0)$ with the energy of the order of $10^{-9}$ Ry, which is not seen in our calculations. It is clear that this state should be discarded.

### 3.6. He$_2^+$: conclusions

Inside of the Born–Oppenheimer approximation by using two-point Padé approximants, analytic expressions for the potential energy curves in the whole range of internuclear distances $R > 0$ are constructed for both the ground $X^2 \Sigma^+_u$ and the first excited $A^2 \Sigma^+_g$ states for the diatomic molecular ion He$_2^+$. In general, the obtained analytic curves reproduce known numerical results with an accuracy of 3–4 s.d. in the whole domain in $R$.

For small internuclear distances $0.5 < R < 1.5$ a.u., possibly due to the quasi-crossing between the excited state $A^2 \Sigma^+_g$ with the next $\Sigma_g$ excited states, the potential energy curve gets inaccurate in this domain of internuclear distances. It leads to a certain loss of accuracy in the spectra of rovibrational states situated in Van der Waals minimum, but it does not change the number of rovibrational states, which is equal to nine. All these states are very weakly-bound.

In the case of ground state $X^2 \Sigma^+_u$ the predicted potential curve through analytic approximation (28) (with the expressions (20) and (26) as building blocks) in the same domain $0.9 < R < 1.5$ a.u. differs from numerical results insignificantly [25]. Probably, it indicates the existence of ‘weak’ quasi-crossing effect. This deviation does not make a significant change in the description of the spectra of rovibrational states obtained with 3–4 s.d. in accuracy. Note the predicted minima by the approximations (28) differ from the numerical results by $\sim 0.1\%$ and $\sim 25\%$ for the ground $X^2 \Sigma^+_u$ and the first excited $A^2 \Sigma^+_g$, respectively.

The obtained analytic expressions for the PEC allow us to solve the radial (nuclear) Schrödinger equation for the nuclear motion of $^4$He$_2^+$ by using the Lagrange-mesh method with an accuracy of 3–4 s.d. The ground state curve $X^2 \Sigma^+_u$ keeps 829 rovibrational states, which is one state less than the 830 states reported in the literature [25], where adiabatic corrections are taken into account. For the excited state curve $A^2 \Sigma^+_g$ the predicted rotational and vibrational states are certainly beyond of the BO approximation and various corrections should be taken into account in order to make definite conclusions. By replacing the nucleus $^4$He by nucleus $^3$He in the radial (nuclear) Schrödinger Equation (32), the rovibrational spectra for diatomics $^3$He$_2^+$ can be calculated. As expected, the number of rovibrational states is significantly reduced.

### Table 3. Molecular ion $^4$He$_2^+$: Rovibrational energies $E_{(v,\nu)} \times 10^{-3}$ Ry for the state $A^2 \Sigma^+_g$ in approximation (28).

| $L$ | $v = 0$ | $v = 1$ | $v = 2$ |
|-----|---------|---------|---------|
| 0   | -9.74   | -1.17   |         |
| 1   | -7.3762 | -0.7944 | -0.0003 |
| 2   | -9.12   | -0.90   |         |
| 3   | -6.30   | -0.42   |         |
| 4   | -5.7289 | -0.1557 |         |
| 5   | -6.11   | -1.17   |         |
| 6   | -4.1381 |         |         |
| 7   | -3.88   |         |         |
| 8   | -2.1200 |         |         |

Note: The second line displays results from [24].

![Figure 4. $^4$He$_2^+$ molecular ion: the histogram of rovibrational states supported by the ground state $X^2 \Sigma^+_u$ as a function of the angular momentum $L$ with $L_{\text{max}} = 58$. In total, there are 829 rovibrational states found in [25] and confirmed in the present paper. The additional weakly-bound state, presented by space filled by dots, is also reported in [25], where adiabatic corrections are included, unlike in the present paper.](image-url)
The calculated rovibrational states \((\nu, L)\) due to the analytic knowledge of PEC (28), allow us to explore radiative transitions between those states as it was done in [9, 29]. Up to our knowledge, radiative transitions for the molecular ion \(\text{He}_2^+\) have not been considered before. It will be done elsewhere.

4. Molecular ion LiH as the example

As an example of the application of our approach to heteronuclear diatomic molecules, let us consider the ground state \(X^1\Sigma^+\) of the LiH molecule. At small internuclear distances, \(R \to 0\) the dissociation energy \(\tilde{E}\) is given by

\[
\tilde{E}_{X^1\Sigma^+} = \frac{2Z_1 Z_2}{R} + \epsilon_0 + 0 \cdot R + O(R^2),
\]

(33)

where \(Z_1 = 3\), \(Z_2 = 1\), and \(\epsilon_0 = E_{\text{Be}} + |E_\infty|\). The energy of the united atom is \(E_{\text{Be}} = -29.33474\) Ry [30] and

\[
E_\infty = E_{\text{H}} + E_{\text{Li}} = -(1.000000 + 14.956120) \text{ Ry},
\]

\[
\text{Ry} = -15.956120 \text{ Ry},
\]

is the so-called asymptotic energy [31]. For large internuclear distances \(R \to \infty\), the energy is given by [32]

\[
\tilde{E}_{X^1\Sigma^+} = -\frac{c_6}{R^6} - \frac{c_8}{R^8} + \cdots,
\]

(34)

where \(c_6 = 133.182\) is the Van der Waals constant. Let us take two-point Padé approximant given by

\[
\frac{1}{R} \text{Pade}[N/N + 5](R),
\]

see (6), choose \(N = 4\),

\[
\tilde{E}_{X^1\Sigma^+}^{[2,2]} = \frac{6 + a_1 R + a_2 R^2 + a_3 R^3 + c_6 R^4}{R \left(1 + a_1 R + a_2 R^2 + \sum_{i=3}^{7} b_i R^i + a_3 R^8 + R^9\right)},
\]

(35)

and impose three constraints

\[
\begin{align*}
\alpha_1 &= (a_1 - \epsilon_0)/6, \\
\alpha_2 &= (6a_2 - a_1 \epsilon_0 + \epsilon_0^2)/36, \\
\alpha_3 &= a_3/c_6,
\end{align*}
\]

(36)

which guarantee that the expansions of \(\tilde{E}_{X^1\Sigma^+}^{[2,2]}\) (35) at small and large internuclear distances reproduces correctly the first three terms for small internuclear distances, \(R^{-1}, R^0\) and \(R^1\) in (33) and the first two terms for large internuclear distances, \(R^{-6}\) and \(R^{-7}\), in (34). Making fit of data [33] with (35) or choosing eight points in

**Figure 5.** PEC for the diatomic molecule LiH from (35) (solid line). Points represent data from [33].

\(ab\ initio\) calculations, which look confident, we find eight free parameters

\[
\begin{align*}
a_1 &= 44744.6, & b_1 &= 2179.81, \\
a_2 &= -28086.2, & b_3 &= 727.108, \\
a_3 &= 2614.80, & b_6 &= -592.941, \\
b_3 &= -6739.29, & b_7 &= 158.198.
\end{align*}
\]

Comparison of fit (35) with parameters (36), (37) with the numerical results from [33] is presented in Table 4 and illustrated by Figure 5. Note that fit reproduces with high accuracy the equilibrium distance \(R_e = 3.015\) a.u., see e.g. [33], without extra tuning, and also its vicinity. Fit predicts that the potential curve vanishes, \(E(R_0) = 0\), at \(R_0 = 1.8954\) a.u., where the dissociation energy is equal to zero. For larger \(R > R_0\) PEC becomes negative.

4.1. Rotational and vibrational states

By solving the radial Schrödinger equation for the nuclear motion (32) with the analytic potential (35), the rovibrational spectra \(E_{(\nu, L)}\) can be obtained. The reduced mass of the \(^7\)LiH molecule is calculated using \(m_{\text{Li}} = 12,786.393\) and \(m_{\text{H}} = 1836.153\) [33]. Following the calculations carried out in Lagrange mesh method, the ground state \(X^1\Sigma^+\) of the diatomics \(^7\)LiH supports 24 vibrational states \(E_{(\nu, 0)}\).

Making a comparison of the spectra of vibrational states \(E_{(\nu, 0)}\) with one presented in [33], one can see that not less than 4 figures are reproduced for \(\nu \leq 7\) as it can be seen in Table 5. However, for \(\nu > 7\) the accuracy is reduced to 3 figures and for some values of \(\nu\) even to 2 figures. We have to note that the state (23, 0), is not reported in [33], however, it is identified in [34].

In total, the ground state \(X^1\Sigma^+\) of the diatomic molecule \(^7\)LiH supports 906 rovibrational states \(E_{(\nu, L)}\). These are presented by the histogram in Figure 6 with
maximum angular momentum is as to the homonuclear case of He
states more than the 883 reported in \([34]\).

In a similar way replacing the nucleus \(^{7}\text{Li}\) by \(^{6}\text{Li}\) and/or hydrogen H (proton) by deuteron or triton one can calculate the rovibrational spectra of diatomics \(^{6}\text{LiH}\) and \(^{6,7}\text{LiD}, ^{6,7}\text{LiT}\). Let us consider, for instance, the isotopologue \(^{6}\text{LiH}\). Taking the nuclear mass of \(^{6}\text{Li}\) as \(m_{\text{Li}} = 10,961.898\) \([28]\), it is found that there are 24 vibrational states \(E_{V,0}\) bonded by the electronic ground state \(X^1\Sigma^+\) with \(V = 0, \ldots, 23\). The maximum angular momentum is \(L_{\text{max}} = 60\). In total, the state \(X^1\Sigma^+\) supports 884 rovibrational states, which one state more than the 883 reported in \([34]\). In a similar way as to the homonuclear case of \(\text{He}_2^+\), with a decrease of the reduced mass in heteronuclear case, the number of rovibrational states and maximal angular momentum are reduced.

### Table 5. Molecule \(^7\text{LiH}\): Vibrational states \(E_{(v,L=0)}\) in the ground state \(X^1\Sigma^+\).

| \(v\) | \(E_{(v,0)}\) [\(\text{Ry}\)] | \(E_{(v,0)}\) [\(\text{cm}^{-1}\)] | \([33]\) |
|-------|-----------------|-----------------|------|
| 0     | -0.17861        | -19600.00       | -19600.57 |
| 1     | -0.16621        | -18240.00       | -18240.34 |
| 2     | -0.15423        | -16925.00       | -16924.98 |
| 3     | -0.14264        | -15653.00       | -15653.58 |
| 4     | -0.13145        | -14425.00       | -14425.30 |
| 5     | -0.12064        | -13238.00       | -13239.37 |
| 6     | -0.11021        | -12094.00       | -12095.19 |
| 7     | -0.10015        | -10990.00       | -10992.19 |
| 8     | -0.09047        | -9927.70        | -9930.00  |
| 9     | -0.08116        | -8905.90        | -8908.41  |
| 10    | -0.07222        | -7924.90        | -7927.45  |
| 11    | -0.06365        | -6984.90        | -6987.43  |
| 12    | -0.05546        | -6086.40        | -6088.98  |
| 13    | -0.04767        | -5230.60        | -5233.15  |
| 14    | -0.04027        | -4419.10        | -4421.65  |
| 15    | -0.03330        | -3654.30        | -3656.91  |
| 16    | -0.02679        | -2939.70        | -2942.32  |
| 17    | -0.02078        | -2279.90        | -2282.68  |
| 18    | -0.01532        | -1681.40        | -1684.62  |
| 19    | -0.01050        | -1152.70        | -1156.46  |
| 20    | -0.00643        | -705.37         | -708.64   |
| 21    | -0.00323        | -354.58         | -357.53   |
| 22    | -0.00108        | -118.73         | -118.21   |
| 23    | -0.00011        | -11.65          | -           |

Note: For the sake of convenience, the 3rd column displays energies in \(\text{cm}^{-1}\) with five figures (1 Hartree \(= 219.474.631363 \text{cm}^{-1}\)). The fourth column displays the results from in \([33]\).

### Figure 6. Diatomic molecule \(^7\text{LiH}\): 906 rovibrational bound states in the ground state \(X^1\Sigma^+\) as a function of the angular momentum \(L\). 905 states found in Shi et al. \([35]\) are confirmed and complemented by 5 additional, weakly bound states, presented by spaces filled by dots, are the result of the present analysis (see text).
domains by using (generalised) two-point Padé approximations, involving a few points in $R$ of order 1 a.u. around minimum of the PEC found via ab initio calculations, leads to amazingly accurate analytic formulas for potential curves. In this formalism, hetero- ($A + B$) and homonuclear ($A + A$) diatomics are conceptually different: the latter ones contain exponentially small terms at large distances due to tunnelling between two identical Coulomb wells, which appears in addition to multipole expansion. It results to the general formula for the approximating the potential curve,

$$V(R) = \frac{1}{R} \text{Pade}(n/m)(R) + \delta_{Z_A,Z_B}\delta_{M_A,M_B}D_0(R)e^{-S_0(R)}\text{Pade}(p/q)(R), \tag{37}$$

where $n, m = n + 3(5), p, q$ are integers, see below, $Z_A, Z_B$ and $M_A, M_B$ are charges and masses of nuclei $A, B$, respectively, $\delta$ is the Kronecker symbol, $D_0, S_0 = \alpha R$ as well as numbers $(p, q)$ depend on the diatomics under investigation. In general, the parameters of the Padé approximants depend significantly on the diatomics we study. It excludes the existence of universal formulas for the potential curves of diatomics for the entire domain of $R$, which is in agreement with conclusions drawn in the book by Goodisman [36], but proclaimed the opposite in Ref. [37].

It has to be emphasised that if we consider heteronuclear diatomics the second term in (37) disappears, we arrive at (5),

$$V_{\text{ion}}(R) = \frac{Z_AZ_B}{R}\text{Pade}(N/N + 3),$$

for positively charged diatomic and at (6),

$$V_{\text{neutral}}(R) = \frac{Z_AZ_B}{R}\text{Pade}(N/N + 5),$$

for neutral one. These formulas look functionally similar, they can be easily used to study any hetero-nuclear diatomics in the whole range of internuclear distances. However, the emerging coefficients in Padé approximants depend on the system at hand and the present authors were unable to see hints indicating to their universal behaviour, at least, so far.

The approach was illustrated by studying the PECs for $^4\text{He}_2^+, ^5\text{He}_2^+, ^7\text{LiH}$ and $^9\text{LiH}$ diatomics. With sufficiently high accuracy the rovibrational spectra is described for both diatomics and its isotopologues. Radiative transitions will be studied elsewhere. It has to be noted that recently in the framework of the present formalism, the overwhelming study of the PEC in the form (6) and the rovibrational spectra was carried for HF, DF and TF molecules [38].

Approximate analytic expressions for the PEC allow to simplify studies of the contribution of BO potential (electronic) curves, which describe two-atom interactions (or saying differently two-body, nucleus-nucleus interactions), into polyatomic potential surfaces at large internuclear distances. It will be studied elsewhere. There exists an interesting possibility to construct the approximate eigenfunctions of the nuclear Hamiltonian, where the analytic PEC plays the role of potential. It is an open direction.

Note added. After submission of this paper for publication, the formula (6) is employed to explore the ground state BO potential curve and the rovibrational spectra of the chlorine monofluoride ClF (ArXiv: 2202.10666, pp.9 (February 2022)). It allowed us to resolve controversy between different ab initio calculations and also with experimental data, and for the first time to calculate the total number of vibrational, rotational, rovibrational states.

Notes
1. Sometimes, in physics literature it is called the Born–Oppenheimer approximation of the zero order.
2. In this consideration it is always assumed that the nuclei are point-like, having no internal structure. We never go to ultra-small distances where strong interaction plays the role and nuclear forces should be considered.
3. Sometimes, it is called the super-ion.
4. The case $n = 1/2$, which corresponds to the $\text{He}_2^+$ molecular ion, will be presented later.

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Disclosure statement
No potential conflict of interest was reported by the author(s).

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