Long-range Rydberg molecule Rb$_2$: Two-electron $R$-matrix calculations at intermediate internuclear distances

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The adiabatic potential energy curves of Rb$_2$ in the long-range Rydberg electronic states are calculated using the two-electron $R$-matrix method [M. Tarana, R. Čurík, Phys. Rev. A 93, 012515 (2016)] for the intermediate internuclear separations between 35 a.u. and 200 a.u. The results are compared with the zero-range models to find a region of the internuclear distances where the Fermi’s pseudopotential approach provides accurate energies. A finite-range potential model of the atomic perturber is used to calculate the wave functions of the Rydberg electron and their features specific for the studied range of internuclear distances are identified.

I. INTRODUCTION

Diatomic long-range Rydberg molecule (LRRM) is an exotic system of two atoms – one in its ground state and one in its high excited state (typically $n \sim 10–80$), bound to each other at the distances of the nuclei varying between tens and thousands of bohrs. The mechanism of this bond consists in the scattering of the Rydberg electron off the distant neutral atom (perturber). This interaction can affect the phase of the Rydberg wave function in such way that the molecular electronic bound state is formed. When its energy, as a function of the internuclear distance, forms sufficiently deep well, the vibrational states of the LRRMs can be bound.

Existence of the LRRMs was first theoretically predicted by Greene et al. [1] almost two decades ago along with their unusually large permanent electric dipole moments, even for the homonuclear diatomic molecules. Two categories of the electronic bound states were identified: Those formed by the perturbation of the non-degenerated atomic Rydberg states with low angular momenta and the trilobite states involving the hydrogen-like degenerated atomic states with high angular momenta. It took almost nine years since then until the first experimental evidence of the LRRMs was provided by Bendkowsky et al. [2] and their electric dipole moment measured by Li et al. [3].

Since then, the LRRMs became a subject of intensive theoretical and experimental research. The trilobite-like states were observed in cesium by Booth et al. [4]. The existence of the butterfly states, predominated by the p-wave interaction of the Rydberg electron with the neutral perturber, predicted by Hamilton et al. [5], was experimentally confirmed by Niederprüm et al. [6]. Although the LRRMs have been so far predominately prepared in the ultracold atomic ensembles of the heavy alkali metals [2, 4, 6], Ding et al. [7] recently reported successful creation of the vibrationally excited LRRMs in the cold strontium gas.

The LRRMs have also provided ways to explore other phenomena. Schmid et al. [8] proposed an experiment where the ionized LRRM Li$_2$ provides a well defined initial state for the Li-Li$^+$ collision in the quantum regime that was not available to previously developed experimental techniques. Deiß et al. [9] utilized the LRRMs Rb$_2$ to study the effects of the spin-orbit interactions in the electron collisions with the rubidium atom at low scattering energies.

Summary of the related research exceeds the scope of this article. For comprehensive review, see the recent paper by Fey et al. [10] and references therein.

The first and so far most frequently utilized theoretical model of the LRRMs is based on the representation of the neutral perturber by the Fermi’s pseudo-potential that couples the atomic eigenstates of the Rydberg electron. This delta-function interaction possesses a singularity at the position of the perturber. It is usually considered non-zero only in the partial waves s and p and parameterized by the generalized energy-dependent electron-perturber scattering length [1, 11] in the s-wave. Following Omont [12], the p-wave component, particularly important for the alkali metals supporting the low-energy $^3P_s$ resonance, is parameterized by the low-energy p-wave phase shift of the electron-perturber scattering [5].

This simple model was more recently enhanced by taking the spin effects into account [13, 14] and provided an insight into several experimental results. One complication inherent to the zero-range model is the irregular behavior of the molecular Rydberg wave function at the location of the perturber due to very singular character of the potential. The fact that this model does not take into account the effects associated with the finite size of the perturber (i.e., its polarization by the other positive Rydberg core) is not a considerable issue in the interval of the internuclear separations where majority of the experiments is performed. The zero-range model also assumes that the classical kinetic energy of the Rydberg electron at the position of the perturber is so small that the approximation of the scattering length [11, 12] or modified effective range [15] is valid. This assumption is also met in majority of the experimentally relevant regimes of the
LRRMs. The first study where the neutral perturber was represented by a finite-range potential, was due to Khuskivadze et al. [10].

The most frequently utilized experimental technique to prepare the LRRMs is their photoassociation in the ultracold atomic ensemble via excitation of the atoms into the Rydberg states (see the review by Shaffer et al. [17] and references therein). The involved atomic states typically possess the principal quantum numbers $n > 30$ and corresponding relevant internuclear distances lie above 200 a.u. [17] where the Fermi’s zero-range model provides quantitatively satisfactory accuracy of the calculated electronic and vibrational energies.

However, Bellos et al. [18] carried out an experiment in which different mechanism was utilized to prepare the LRRMs $\text{Rb}_2^+$. First, weakly bound $\text{Rb}_2$ molecules in their lowest excited electronic and high vibrational state $|a^3\Sigma_u^+, \nu = 35\rangle$ were photo-associated in the magneto-optical trap containing ultra-cold rubidium atoms. The LRRMs with the energies between the states $5s + 7p$ and $5s + 12p$ (in the asymptotic limit of the separated atoms) were then directly photo-excited. The information about the populations of different electronic and vibrational energy levels of the LRRMs was retrieved using the autoionization spectroscopy of the molecular cations $\text{Rb}_2^+$. Later, the states slightly red-shifted with respect to the $5s + 7p$ energy were studied in more detail by Carollo et al. [19].

The outer vibrational turning point of the initial molecular state $|a^3\Sigma_u^+, \nu = 35\rangle$ is approximately at the internuclear separation $\approx 35$ a.u. and relatively low Rydberg energies are populated by the subsequent photoexcitation. As a result, the LRRMs prepared by Bellos et al. [18] possess significantly lower internuclear separations than those produced via the direct photoassociation of the atomic pair utilized in majority of other experiments.

Although Bellos et al. [18] successfully associated some of the features observed in their experimental spectra with the structures in the potential energy curves (PECs) calculated using the Fermi’s pseudo-potentials [13], the validity of this model becomes questionable at these small internuclear separations and low energies. Since the size of the perturber is not negligible compared to its distance from the Rydberg atomic core, their mutual interaction may become relevant. Similarly, the size of the perturber is not negligible compared to the de Broglie wave length of the Rydberg electron.

In order to address the validity of the zero-range model of the LRRMs at small internuclear distances, this article is dealing with the PECs of $\text{Rb}_2$ calculated using different models. The calculations are focused on the intermediate range of the internuclear separations below 200 a.u., similar to that studied by Bellos et al. [18]. A complex approach, suitable for this range of the nuclear distances, where the valence electron of the alkali-metal atomic perturber is explicitly represented as well as the Rydberg electron, was formulated by Tarana and Čurík [20] (hereafter referred to as TC). The Coulomb potential of the positive Rydberg atomic core is also taken into account. The construction of this model for $\text{Rb}_2$ is discussed in the present article along with the comparison between the obtained PECs and those published by Bellos et al. [18] to establish the range of the internuclear distances where the zero-range model provides quantitatively accurate results.

This paper presents the first application of the two-electron $R$-matrix approach [20] to other molecular system than $\text{H}_2$. Another goal of this work is to present the PECs associated with the perturber in its excited state as these exist below the ionization energy in $\text{Rb}_2$ and can be calculated using the approach developed in TC.

The probability densities of the Rydberg electron are also presented in terms of a one-particle finite-range model of the LRRMs [16] in order to understand their features that are specific to the range of the distances between the nuclei studied in this work.

The spin-orbit couplings and spin-spin couplings are not considered in the calculations presented here. Although their effects can be experimentally recognized in the heavy alkali metals [9, 17, 21], the phenomena investigated in this article are not directly related to the relativistic effects. Adding corresponding degrees of freedom to the two-electron $R$-matrix method formulated in TC would, for the study presented here, yield computationally more demanding calculations without providing equivalent additional insight into the underlying mechanisms.

The rest of this article is organized as follows: The model potential of $\text{Rb}_2^+$ and corresponding quantum defects are discussed in Section II. Sections III and IV are dealing with the parameters of the two-electron and one-electron $R$-matrix calculations, respectively. The results of the calculations are analyzed in Sections V and VI. The conclusions are formulated in Section VII.

Unless explicitly stated otherwise, the atomic units are used throughout the rest of this article.

II. REPRESENTATION OF Rb AND Rb$^+$

The notation of TC was adopted in this section. In the two-electron $R$-matrix method formulated by Tarana and Čurík [20], the positive atomic core of the neutral perturber $A$ is represented by a potential $V_A(r)$. Its parameters are optimized to reproduce the energies $\varepsilon_{nl}$ of the ground and excited states of the neutral atom (see TC Eqs. (8)), where $n$ and $l$ denote the principal quantum number and angular momentum of the electron, respectively. Following Marinescu et al. [22], an $l$-dependent potential $V_A^{(l)}(r)$ was used for $l \leq 3$ to represent the positive core $\text{Rb}_2^+$. Although the $l$-dependence of $V_A^{(l)}(r)$ was not explicitly assumed in TC, it does not represent any practical difficulty.

The model potential utilized in the calculations pre-
was optimized for several lowest states with $r_0$ and is the static dipole polarizability of Rb$^+$. The spin-orbit interaction is larger than the accuracy with $Z$ where $A_l \ldots B_l$ and $r_{cl}$ are the fitting parameters. The potential $V_A^{(l)}(r)$ was optimized for several lowest states with $l = 0 \ldots 3$ to match the corresponding experimental energies [24].

The optimization of $V_A^{(l)}(r)$ was for the rubidium atom performed in the same way as was discussed by Tarana and Ćurik [25] for lithium. The obtained values of the parameters are summarized in Table I. The largest difference between the $j$-averaged experimental energy [24] and corresponding value obtained using $V_A^{(l)}(r)$ among the states used for the optimization, was smaller than 0.5 cm$^{-1}$.

In addition to the low lying states of Rb, $V_A^{(l)}(r)$ yields accurate energies of the higher excited states that were not involved in the optimization procedure. This was verified by the calculation of the corresponding energy-dependent quantum defects $\mu_l(\varepsilon)$ for the negative energies and by their comparison with the experimental results previously published by Lorenzen and Niemax [26]. Since the positive core $B$ of the Rydberg atom is in the two-electron $R$-matrix method represented by the quantum defects [10], this agreement shows that both cores $A$ and $B$ are treated consistently with each other.

### TABLE I. Optimized values of the parameters in Eq. (1).

| $l$ | $\beta_0$ | $\beta_1$ | $\beta_2$ | $r_{cl}$ |
|-----|-----------|-----------|-----------|----------|
| 0   | 4.58399   | 16.3777  | 1.91381   | 1.23006  |
| 1   | 4.67960   | 17.6441  | 1.94827   | 1.31018  |
| 2   | 4.40538   | 15.5548  | 1.95719   | 1.20402  |
| 3   | 3.93385   | 27.7401  | 2.19395   | 2.58766  |

The energy splitting of the excited states due to the spin-orbit interaction is larger than the accuracy with which these states can be obtained using $V_A^{(l)}(r)$. Since the spin-orbit coupling is not considered in this study, the pairs of the experimental energies [24] within the $nl$ manifold with $j = l \pm 1/2$ were $j$-averaged (for $l > 0$) and subsequently used to fit $V_A^{(l)}(r)$. The parameters in Eq. (1) were fitted to match lowest 6, 5, 5, 5 $j$-averaged energies of the states with $l = 0, 1, 2, 3$ respectively. The eigenenergies of the states with $l > 3$ are very close to those of the hydrogen atom and the corresponding model potential was set to $V_A^{(l>3)}(r) = -1/r$.

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In order to treat the polarization effects between the Rydberg electron and the valence electron of the neutral perturber accurately, the radius of the $R$-matrix sphere centered at the core $A$ was set to $r_0 = 30$ a.u. The test calculations with larger radius 33 a.u. showed negligible difference in the obtained PECs. The formulation of the $R$-matrix method [20] assumes that the polarization potential of the perturber can be neglected outside the $R$-matrix sphere. Therefore, larger $r_0$ allows for larger portion of the polarization potential included in the calculation.

It is well known that in order to treat the electron scattering off the alkali metals accurately at very low energies that are relevant in this study, it is necessary to propagate the wave function in the polarization potential to very large distances [27]. In order to converge the phase shifts at the low energies, thousands of atomic units are typically necessary [25, 27]. This is due to their large polarizability and the polarization potential affecting the phase of the scattering wave function even at large distances from the target. However, in the LRRMs, except relatively small vicinity of the perturber, it is the Coulomb tail of the Rydberg core $V_B(|\mathbf{r} - \mathbf{R}|)$ that dominates over the polarization potential of the perturber and its effect is treated accurately by the Coulomb Green’s function [16, 20, 28] (the position vector of the core $B$ with respect to the core $A$ is denoted as $\mathbf{R}$ and the internuclear distance is denoted as $R$). Therefore, the calculations of the LRRMs PECs performed with $r_0 = 30$ a.u. yield very accurate energies although the same radius would not be sufficient to provide accurate scattering phase shifts at low energies without additional propagations.
tion of the wave function in the polarization potential outside the \( R \)-matrix sphere.

The radial basis set of 86 \( B \)-splines of the 8th order was defined inside the \( R \)-matrix sphere on knot sequence spanning the interval \([0, r_0]\). It was divided into three subintervals with equidistant separation of the knot points in each of them: 10 knots were used in the subinterval \([0, 1/37]\) a.u., set of 10 knots was used in the subinterval \([1/37, 2]\) a.u. and 60 points uniformly spanned the remaining interval to the surface of the \( R \)-matrix sphere.

The angular basis set used inside the \( R \)-matrix box (see TC Eq. (6)) consists of the eigenstates \( \psi_{l_1 l_2}^{(LM)} \) of the total two-electron angular momentum with quantum numbers \( L \) and \( M \). The one-particle angular momenta of the individual electrons are denoted as \( l_1 \) and \( l_2 \). A wider range of the angular momenta was included in the basis set for the calculation performed at smaller internuclear separation \( R \) than for those at bigger \( R \). The reason is that the Coulomb tail of \( V_B \) that breaks the overall spherical symmetry of the two-electron system, varies within the \( R \)-matrix sphere more rapidly at smaller \( R \). As a result, components of the wave function with higher angular momenta are required to converge the calculation. The basis functions with \( l_1 l_2 \leq 5 \) were used for \( R \geq 60 \) a.u. For 60 a.u. > \( R \geq 45 \) a.u., the angular basis set was extended to \( l_1 l_2 \leq 6 \) and to \( l_1 l_2 \leq 7 \) for the internuclear distances below 45 a.u.

Every extension of the angular space significantly increases the size of the Hamiltonian matrix \( H' \). This raises the issues with the computer memory and time necessary for its construction and diagonalization. In order to keep the calculations computationally tractable, the angular space was extended only at smaller values of \( R \) where it is necessary instead of employing the largest basis set in whole range of \( R \) investigated in this study.

The high computational demands of inner-region calculations in cases when the nuclei approach each other restrict the research of the PECs to \( R \geq 35 \) a.u. More fundamental lower limit of the internuclear distances at which the \( R \)-matrix method can be applied, is the radius of the \( R \)-matrix sphere \( r_0 \). The presence of the positive core \( B \) inside the \( R \)-matrix sphere would require its different representation and consequently reformulation of the inner-region treatment.

In addition to the potential \( V_{\text{core}}^{(i)} \) and electron-electron repulsion, the dielectric term \( V_{\text{dielectric}} \) was added to the two-electron Hamiltonian \( \hat{H} \) (TC Eq. (2)) in order to treat the interaction between the Rydberg electron and neutral perturber more accurately. This term accounts for the interaction between the valence and Rydberg electrons via the dipole and quadrupole moments induced on the core \( A \). The explicit form of this term utilized in this study as well as the optimization of the parameters are identical to those described by Tarana and Čurík [25] for the lithium atom. In addition to the static dipole polarizability of the \( \text{Rb}^+ \) core \( \alpha_{dc} = 9 \) a.u. [23], the dielectric correction is parametrized by the quadrupole polarizability of \( \text{Rb}^+ \) \( \alpha_{q} = 35.4 \) a.u. [31] and by the cutoff radius \( r_c = 1 \) a.u. optimized to accurately reproduced the electron affinity of \( \text{Rb} \).

As it is discussed in TC, the two-electron configurations in the close-coupling expansion of the wave function (TC Eq. (6)) involve two categories of the one-electron radial orbitals: The open orbitals represented by all the \( B \)-splines and the closed orbitals \( u_{\text{qc}}(r) \) – the lowest bound states of the bare perturber. The states 5s, 5p, 4d, 6s and 6p of rubidium were used as the closed orbitals in the calculations presented here. Further extension of this set did not change the obtained results.

Four lowest eigenstates \( \varphi_{im_1}(r_1) \) of the perturber in the Coulomb tail of the potential \( V_B(r - R) \) were included in the calculations as the scattering channels (see TC Eqs. (3), (4) and (18)). They correspond to the ground state 5s of \( \text{Rb} \) and triply degenerated lowest excited state 5p split by the non-spherical off-center Coulomb potential \( V_B \). They are essential for the calculation of the PECs involving the excited states of the perturber.

The solutions of the Schrödinger equation outside the \( R \)-matrix sphere, where the Coulomb tail of \( V_B \) predominates, are expressed in terms of the Coulomb Green’s function [28]. The additional term to account for the non-hydrogenic character of the Rydberg core \( B \) derived by Davydkin et al. [32] is included. In that correction term, the positive core is characterized by the quantum defects \( \mu_i \) in those partial waves (with respect to the core \( B \)) where these are not negligible. In case of rubidium, the Rydberg-center angular moments up to \( l = 3 \) were considered (see Fig. 1). Technically, this correction of the Coulomb Green’s function appears in the integrals for the elements of the matrices \( \Gamma \) and \( \Gamma' \) (see TC Eqs. (37)). They express the condition for the smooth matching of the inner-region and outer-region wave functions on the \( R \)-matrix sphere.

**IV. ONE-ELECTRON \( R \)-MATRIX CALCULATIONS**

The multidimensional character of the electronic wave function inside the \( R \)-matrix sphere taken into account in the two-electron \( R \)-matrix method [29] limits its possibilities to visualize this wave function. Although the single-particle wave function of the Rydberg electron can be easily plotted in the outer region (TC Eq. (29)) that is most important for this study, that information is not sufficient at the energies and internuclear distances discussed in this paper as the size of the \( R \)-matrix sphere is comparable with the size of the overall region where the Rydberg electron can be located.

In order to investigate the features of the Rydberg wave functions, another single-particle model of the LR-RMs was utilized where the perturber was represented by a finite-range potential. Although this model is less complex than the two-electron treatment, the PECs obtained from both approaches (discussed in Section [VI]) are in good qualitative agreement. In addition, the wave
functions calculated using the finite-range single-particle model do not show the artifacts associated with the singularities in the zero-range potentials.

The finite-range potential representing the neutral rubidium perturber in the single-particle part of this study was constructed by Khuskivadze et al. [10] and successfully utilized in the context of the LRRMs [10] as well as the near-threshold photodetachment of the alkali metal anions [33]. It was optimized to accurately reproduce the low-energy phase shifts of the e−−Rb collisions (the same constraint as in the case of the zero-range potentials – see [21] and the references therein). The interaction between the electron and neutral rubidium is considered in the partial waves s and p, in both singlet and triplet spin symmetries.

Although Khuskivadze et al. [10] also included the spin-orbit term in their potentials, these were disregarded in the one-particle part of this work in order to construct the model that is more consistent with the two-electron approach where this interaction is neglected.

The computational method used to obtain the energies of the electronic bound states of the LRRMs is also similar to that of Khuskivadze et al. [10] where the configuration space of the Rydberg electron is separated by a sphere centered on the perturber and sufficiently large so that the interaction of the Rydberg electron with the perturber can be neglected outside where the wave function is expressed in terms of the Coulomb Green’s function [28] with the correction for the quantum defects of the Rydberg core [32]. In the calculations presented here, the Schrödinger equation inside the R-matrix sphere was not directly numerically integrated for every energy of the interest as in the reference [10]. Instead, the problem was in the inner region formulated in terms of the $R$ matrix and treated along the same lines as in TC. The fact that this model involves only single electron makes the formulation and numerical implementation much more simple than in the two-electron case while the wave functions of the $\Sigma$-states can be plotted as two-dimensional maps inside as well as outside the $R$-matrix sphere.

The spherical harmonics $Y_{l,m}$ with $l = 0 \ldots 7$ and $m = 0$ were used as an angular basis in the inner region where the wave function was expanded with respect to the center of the sphere. Although the interaction with the perturber is not considered for $l > 1$, the off-center Coulomb potential due to the Rydberg core requires the higher angular momenta, particularly at smaller internuclear separations.

The radius of the $R$-matrix sphere was in the single-electron calculations set to 30 a.u. The radial part of the wave function was expressed as a linear combination of 200 $B$-splines of the 6th order spanning the interior of the $R$-matrix sphere with increasing density of the knots towards the center of the sphere.

Using this basis set in the inner region, the energy-dependent $R$-matrix was calculated on the sphere. Following TC, the energies of the bound electronic states were identified as those for which is $R$-matrix is compatible with the logarithmic derivative of the wave function calculated on the sphere using the Coulomb Green’s function in the outer region.

Corresponding Rydberg wave functions can be technically evaluated everywhere in the space. However, the small vicinities of both atomic centers require specific attention and the probability densities in those small regions were not studied in this work. Since the Coulomb Green’s function with the correction for the non-hydrogen core [32] involves the irregular Coulomb function, the solution of the Schrödinger equation propagated using this Green’s function shows unphysical increase in the small vicinity of the Rydberg core ($\approx 4$ a.u. for Rb$^+\). However, this region is in reality occupied by the atomic ion. Therefore, the Rydberg wave function cannot be expressed there as a linear combination of the regular and irregular Coulomb functions.

The wave function in the close vicinity of the center of the neutral perturber ($\approx 4$ a.u. for Rb) shows rapid unphysical oscillations with large amplitudes due to very attractive character of the model potentials [10] near the center. However, this region is in reality also occupied by the electrons of the perturber and the wave function does not have single particle character. The model potential was optimized to reproduce the wave function correctly at larger distances from the atomic center where the other electrons of the atom do not appear.

V. POTENTIAL ENERGY CURVES

The $^3\Sigma$ PECs of the long-range Rydberg states in Rb$_2$ were calculated using the two-electron $R$-matrix method for the internuclear distances $R$ between 35 a.u. and 200 a.u. The energies of our interest span the interval between the dissociation thresholds corresponding to the states of the non-interacting atoms $5s + 7p$ and $5s + 13p$. These PECs are plotted in Figs. 2, 3 and 4. Small segments of several PECs in these plots are missing near the energies corresponding to the infinite separation of the nuclei. It is due to the finite energy grid used in the numerical matching of the wave functions on the $R$-matrix sphere. In cases when the points are not plotted in Figs. 2, 3 and 4, the energy grid is not sufficiently fine to separate the molecular states where det$(M) = 0$ (see TC Eq. (38)) from the energies of unperturbed atomic Rydberg states where the Green’s function possesses poles.

Among the other curves discussed below, Figs. 2 and 4 also show three very steeply raising PECs that do not appear in the results obtained using the zero-range model potentials. They are artifacts of the utilized computational method that are further explained in Appendix.
FIG. 2. PECs $^3\Sigma$ calculated using the two-electron $R$-matrix technique (black dotted lines) compared with the curves obtained from the zero-range model by Bellos et al. [18] (red dashed lines). Zero energy corresponds to the system of two non-interacting Rb atoms in the state 5s. The marks on the right side of the graph denote the electronic states of the non-interacting atoms at infinite separation. The vertical arrows inside the graph denote the degenerate hydrogen-like manifolds with angular momentum of the Rydberg electron $l > 3$.

A. Comparison of the two-electron $R$-matrix results with the zero-range model

In Fig. 2 the potential curves calculated using the two-electron $R$-matrix method are compared with those obtained by Bellos et al. [18] where the perturber is represented by the zero-range potential in the partial waves $s$ and $p$. Both approaches yield qualitatively similar results. The differences become visible near the crossings of the PECs with each other. More significant disparities appear in the regions where the PECs detach from the degenerate hydrogen-like manifolds $5s + n(l > 3)$ ($n = 7 \ldots 10$, denoted by the vertical arrows in Figs. 2 and 4) and descend via series of avoided crossings as $R$ decreases. Their ion-pair-like character is due to the low-energy $p$-wave resonance in Rb$^-$ [5, 30, 34]. In this regime, the probability density of the Rydberg electron is localized around the perturber more than in the general molecular Rydberg states. It suggests that the differences between the PECs compared in Figs. 2, 3, and 4 is caused by different treatment of the $p$-wave interaction between the perturber and the Rydberg electron. The zero-range potential is constructed to yield the same low-energy phase shifts as the true multi-electron interaction. The two-electron $R$ matrix takes into account not only the full repulsion between the Rydberg electron and the valence electron of the perturber, the influence of the positive core $B$ on the valence electron of the neutral atom is included as well. The two-electron $R$-matrix method also does not depend on the assumption that the local kinetic energy of the Rydberg electron at the position of the perturber is small. These subtle effects can play an important role in the states where the Rydberg electron is predominately localized in the vicinity of the perturber.

Another region where the two-electron $R$-matrix PECs deviate from those calculated using the Fermi-type model [18] is $R < 40$ a.u. It is particularly well visible in Fig. 3 for the PEC with the asymptotic energy $5s + 7p$. The polarization of the perturber by the positive core $B$ gradually gains importance in this region as the internuclear distance decreases. While this effect is included in the two-electron $R$-matrix treatment (see TC Eqs. (2) and (3) as well as TC Appendix A), the zero-range approach [18] disregards any interaction between the perturber and the positive core of the Rydberg atom. The raising influence of this effect at smaller internuclear distances is evident from the fact that in order to converge the $R$-matrix calculations, increasingly higher one-particle angular momenta are necessary in the close-coupling expansion TC Eq. (6) for decreasing $R$.

This range of small $R$ is relevant in the context of the experimental studies by Bellos et al. [18] and Carollo et al. [19]. The authors attempt to identify the Rb$_2$ LR-RMs for $R \lesssim 50$ a.u. by associating the peaks observed in the vibrational spectra of the Rydberg molecules with the structures in the calculated zero-range PECs. The differences at $R < 40$ a.u. between the PECs presented here and those published in the reference [18] suggest that other interpretation of the experimental spectra than proposed in the references [18, 19] might be plausible.

This can be illustrated on the electronic state with the asymptotic energy $5s + 7p$ that is subject of the detailed analysis by Carollo et al. [19]. Corresponding zero-range PEC, displayed in Fig. 3 shows a potential barrier and a potential well. Carollo et al. [19] calculated the vibrational states localized left of the barrier (inner states) and inside the potential well (outer states). Their vibrational energies were assigned to the observed peaks in the experimental spectra and the long-range Rydberg states were, depending on their localization, characterized as inner or outer.

However, as can be seen in Fig. 3 the two-electron $R$-matrix calculations yield the part of the potential well, that is treatable by this method, deeper and raising more steeply than the zero-range model. It is possible that more complex approach to the calculations of the PECs for even smaller distances of the nuclei would provide different spectrum of the vibrational states in this region. Consequently, this might change the interpretation of the spectra measured by Carollo et al. [19].
B. PECs associated with excited perturber

The two-electron $R$-matrix method allows for calculation of the PECs associated with the excited states of the perturber as its valence electron is directly represented. In the limit of infinitely separated nuclei, three dissociation thresholds involving the perturber in its excited state lie below the lowest ionization threshold: $5p + 5p$, $5p + 4d$ and $5p + 6s$. The lowest ($5p + 5p$) and highest ($5p + 6s$) among them lie below and above the energy interval studied in this article, respectively. The PECs with the asymptotic energy corresponding to the separated atomic states $5p$ and $4d$ are displayed in Figs. 2 and 4. The computations were performed in such a way that the atom in the state $5p$ was placed inside the $R$-matrix sphere as the perturber. Technically, its excited state was represented as a closed scattering channel.

Since the excitation energy of the perturber represents here a large portion of the total energy, the Rydberg electron is confined deeper in the potential $V_B$ (see TC Eq. (2) and TC Fig. 2) than in the molecular states where the perturber is in its ground state. As a result, the potential barrier formed by the Coulomb tail of $V_B$ and polarization potential of the perturber in its excited state is too high for the Rydberg electron to classically reach the perturber for every internuclear separation considered in this work. Therefore, all the segments of the PECs associated with the excited perturber located at $R \gtrsim 43$ a.u. can be very accurately approximated as

$$E(R \gtrsim 43 \text{ a.u.}) = \epsilon_{2m_1}(R) + \epsilon_{42},$$

where $\epsilon_{42}$ is the energy of the atomic Rydberg state $4d$ given by TC Eqs. (8) and $\epsilon_{2m_1}(R)$ are the energies of the perturber in the excited state $5p$ polarized by the Coulomb tail of $V_B$ (see TC Eqs. (3) and (4)). The triply degenerated state $5p$ of the perturber is split by $V_B$ into the lower state with $m_1 = 0$ and the higher doubly degenerated state where $m_1 = \pm 1$. The angular momenta of the Rydberg electron are then coupled in such a way that the projection of the total angular momentum on the internuclear axis $M = m_1 + m_2 = 0$. Following TC, the projection of the Rydberg electron angular momentum on the internuclear axis is denoted as $m_2$.

Validity of this approximation breaks at $R \lesssim 43$ a.u. where the lower PEC shows clear minimum and the higher doubly degenerated anti-bonding curve shows even more steep anti-bonding character. Although the lower curve supports the bound vibrational states, their experimental realization or observation might be generally difficult due to low lifetimes of the involved low excited atomic states \[35\].

VI. RELATION BETWEEN RYDBERG WAVE FUNCTIONS AND STRUCTURES IN PECs

The structures in the calculated PECs are related to the character of corresponding electronic wave functions. Despite their high symmetry, the two-electron wave functions obtained from the $R$-matrix calculations are complicated to analyze, especially inside the $R$-matrix sphere. In order to explore the structure of the Rydberg electron wave functions, the finite-range model of the interaction between the neutral perturber and Rydberg electron developed by Khushkivadze et al. \[16\] was utilized to perform the single-electron $R$-matrix LRRM calculations with well-defined one-electron wave functions. The PECs obtained in this way overall compare to those calculated by Bellos et al. \[18\] very well (this comparison is not visualized in this article). The agreement is better than between the two-electron $R$-matrix results and the zero-range model. It is not surprising provided that both, the finite-range and zero-range model, are constructed to
correctly reproduce the same characteristics of the $e^{-}$-Rb scattering, specifically the low-energy phase shifts in the partial waves $s$ and $p$.

As can be seen in Fig. 4, the one-electron finite-range model yields PECs qualitatively very similar to those obtained from the two-electron approach. Therefore, it is reasonable to anticipate that the structures found in the corresponding wave functions of the Rydberg electron are also qualitatively correct and allow for the characterization of the two-electron PECs.

The overall qualitative agreement among the PECs calculated using all three models discussed in this article implies that, except small $R \lesssim 40$ a.u., the features discussed in the rest of this section are not consequences of the finite size of the perturber. In fact, as it is discussed below, they can be, at least qualitatively, explained in terms of the zero-range model. They are specific for the range of the energies and internuclear separations discussed in this work.

### A. PECs with asymptotic energies $5s+ns$, $5s+nd$ and $5s+nf$

The first type of the PECs plotted in Figs. 2 and 4 is represented by the curves with the asymptotic dissociation energies corresponding to the atomic states $5s + ns$, $5s + nd$ and $5s + nf$. Except for avoided crossings with the ion-pair-like curves discussed below, these PECs do not significantly depart from their asymptotic energies with decreasing $R$.

Oscillatory structures are present in these curves. Their amplitudes become smaller with increasing energy and the oscillations are more pronounced in the case of the perturbed $d$-states of the Rydberg atom than in the case of the $5s + ns$ and $5s + nf$ PECs. The latter possess too small amplitudes to be recognized in Figs. 2 and 4. The detail between the thresholds $5s + 11d$ and $5s + 13s$ is magnified in Fig. 5. The principles illustrated on these states are valid for all the Rydberg states $ns$, $nd$ and $nf$ investigated in this work. Although the energy variations are small on the scale of the energies studied in this work, it is interesting to discuss them as they show a relation between the current results and the well established zero-range model of the $e^{-}$-Rb interaction [1, 5].

As it is illustrated in Fig. 5, the positions of the local maxima and minima in the PECs agree with the locations of the radial nodes and local extremes in corresponding unperturbed atomic Rydberg wave functions, respectively. As can be seen in the maps of the Rydberg electron densities plotted in Fig. 6, the perturber affects the probability density of the Rydberg electron most significantly locally inside the $R$-matrix sphere. Outside, the wave functions approximately retain their atomic character. At internuclear distances $R$ corresponding to the maxima of the PECs, the $p$-wave component (with respect to the perturber) predominates the wave function inside the sphere (see Fig. 5(b) and (d)). This agrees with the picture provided by the zero-range potential model [1] where the $s$-wave interaction becomes negligible at those positions of the perturber where the probability density of the unperturbed Rydberg electron vanishes.

Similarly, at internuclear distances $R$ where the PECs attain their local minima, the wave function of the Rydberg electron inside the sphere shows predominately $s$-wave character (see Figs. 6(a) and (c)). This also fits in the picture provided by the zero-range potential model: The unperturbed probability density of the Rydberg electron reaches its maximum at these values of $R$ leading to the raise of the $s$-wave electron-perturber interaction. At the same time, the gradient of the unperturbed electronic wave function is negligible at these points along with the $p$-wave interaction of the electron with the perturber [5]. The analysis of the radial molecular wave functions (not displayed here) confirmed that the dominance of the $s$-wave or $p$-wave interaction between the Rydberg electron and the perturber at the significant points, as it is discussed above, is common for the Rydberg states $ns$, $nd$ and $nf$, although it is not apparent from Fig. 6.

Outside the $R$-matrix sphere, the perturbed atomic Rydberg states $ns$, $nd$ and $nf$ are predominated by their spherically symmetric, $d$-symmetric and $f$-symmetric component (with respect to the positive core), respec-
FIG. 6. Two-dimensional maps of the Rydberg electron probability densities in the molecular states where the atomic states $13s$ and $11d$ are modified by the perturber are plotted in the subfigures (a), (b) and (c), (d), respectively. The perturber is located in the center of the coordinate system and the white circle denotes the $R$-matrix sphere. The internuclear distances are marked on the vertical axes and corresponding points on the PECs are labeled in Fig. 5.

This is due to the fact that in rubidium, the states with angular momentum $l < 4$ are not degenerate. As long as the effect of the neutral perturber is small, the contributions of the atomic states with different angular momenta to the total wave function is perturbative.

B. PECs with asymptotic energies $5s + np$ and $5s + n(l > 3)$

The PECs with the asymptotic energies $5s + np$ and $5s + n(l > 3)$ are depicted in Fig. 7, where three curves appear at the energies close to every asymptote $5s + np$: Two of them (denoted as $\alpha$ and $\beta$ in Fig. 7) cross each other and show clear oscillatory behavior. The third curve (denoted as $\gamma$ in Fig. 7) is monotonically decreasing towards the nearest lower asymptotic degenerated hydrogen-like threshold $5s + n(l > 3)$. The amplitudes of the oscillations in the category of the PECs $\alpha$ and $\beta$ are largest among those occurring in this work. Although the discussion in the rest of this subsection is focused on the curves near the $5s + 12p$ threshold magnified in Fig. 7, it is valid for all the Rydberg states $np$ considered in this article.

At large internuclear separations, its wave function (not visualized here) has overall $p$-symmetry (with respect to the Rydberg core) with single angular node. The part of the wave function perturbed by the neutral atom is confined inside the $R$-matrix sphere. At internuclear separations below the avoided crossing between the weakly perturbed state $np$ mentioned above and the ion-pair-like PEC ($R \lesssim 140$ a.u. in Fig. 7), none of the wave functions can be characterized as predominated by the $np$ states (see Fig. 8). Instead, the Rydberg electron wave functions associated with all three PECs have complicated structure with significant contributions of the higher angular momenta. Correspondingly, Fig. 7 shows that the local minima and maxima of the oscillations in the PECs do not accurately correspond to the extremes and zeroes of the radial atomic Rydberg wave function.

The character of the PECs $\alpha$, $\beta$ and $\gamma$ in Fig. 7 can be partially explained by the coupling of the degenerated hydrogen-like manifolds by the neutral perturber represented by the zero-range model. Corresponding pseudopotential of the perturber in the partial waves $s$ and $p$ yields in the basis of the degenerated states with fixed $n$ the matrix of rank two. Therefore, for large $R$ where the perturber does not couple the atomic Rydberg states with different energies, two PECs detach from the degenerated unperturbed asymptote.

One of them descends with decreasing internuclear distance $R$ via a series of avoided crossings with the PECs...
FIG. 8. Two-dimensional maps of the Rydberg electron probability densities in the molecular states where the atomic states 12p and 10(l > 3) are perturbed. The perturber is located in the center of the coordinate system and the white circle denotes the R-matrix sphere. The internuclear distances are marked on the vertical axes and corresponding points on the PECs are labeled in Fig. 7.

discussed in Section VIA as the ion-pair-like curve due to the low-lying e−-Rb resonance [30]. At smaller internuclear separations where the classical kinetic energy of the Rydberg electron in the vicinity of the perturber exceeds the resonance energy, this PEC (curve β in Fig. 7) shows the oscillatory structure similar to that predicted by Hamilton et al. [5]. The authors in reference [5] studied higher excitations of the Rydberg atoms where the oscillatory segments of these deeply bound PECs are well separated from the other asymptotic thresholds 5s + nl. However, for the range of the excited states studied in this work, the oscillating PECs are intersected by the asymptotic energy of the nearest atomic state np lying below the degenerated high-l manifold. This suggests that this state np is coupled to the nearest degenerated manifold above it. Therefore, its perturbation by the neutral atom cannot be treated separately from the deeply bound high-l states. As a result, the weakly perturbed atomic Rydberg states np, consistent with those discussed in Section VIA are absent.

This statement was verified by performing a set of the test one-electron R-matrix calculations where the model potential representing the perturber [10] was artificially made more attractive. Consequently, the oscillatory structures in the high-l PEC β descended towards lower energies while separating from the curve α. The amplitudes of the oscillations in the curve α decreased and its local extremes became consistent with the nodes and extremes of the radial atomic wave function in the same way as discussed in Section VIA for the states ns, nd and nf. At the same time, the Rydberg wave functions corresponding to the points the modified curve β gained clear p-character with the perturbed part of the wave function localized inside the R-matrix sphere.

Therefore, the interaction between the non-degenerated states np and high-l degenerated states is related to the fact that their energy separation is similar to the shift due to their coupling by the neutral perturber.

Note that, in agreement with the results of Hamilton et al. [5], the states corresponding to the PECs α and β in Fig. 7 are predominated by the p-wave interaction of the Rydberg electron with the perturber (see Fig. 8(a)–(d)). On the other hand, the structure of the electron density does not remind the shape of a butterfly that is characteristic for the higher states [21]. This difference in shape also implies that for the states discussed here, the average position of the Rydberg electron is found between the neutral perturber and positive core while, according to Niederprüm et al. [6], in the higher butterfly states, it is located beyond the neutral perturber.

It is interesting that the probability density functions along one of the PECs α or β feature a localized region between the positive core and neutral perturber with very small value of the wave function (Fig. 8(a) and (d)).

C. Trilobite-like states

As it is mentioned above, the perturbation of the degenerated hydrogen-like manifold nl by the zero-range potential in the partial waves s and p results in the detachment of two PECs at large R where the perturbation is weak. One of them is descending with decreasing R as the ion-pair-like PEC discussed above (curves α, β in Fig. 7). The dominant component of the corresponding wave functions in the vicinity of the perturber is the p-wave. The other non-degenerated curve monotonically
to the Ramsauer minimum in the triplet $s$-wave $e^-$-Rb phase shift. The repulsive character of the electron-atom interaction at $R < R_{\text{RM}}^{(nl)}$ consequently yields repulsive PEC.

In order to elucidate the absence of the bound vibrational states associated with the trilobite electronic wave functions emerging from the calculations presented here, an artificial one-electron $R$-matrix calculation was performed where only the $s$-wave $e^-$-Rb interaction was considered. The detail of the calculated PECs near the dissociation thresholds $5s + 9f$ and $5s + 9(l > 3)$ is plotted in Fig. 9(a) by the blue crosses. This artificial trilobite-like PEC has a single shallow minimum below the dissociation threshold $5s + 9(l > 3)$ at $R \approx 148$ a.u. This suggests that in the range of energies and $R$ considered in this study, the nuclear attraction due to the low-energy $s$-wave $e^-$-Rb interaction is so weak that it is compensated by the repulsive effect of the $p$-wave interaction included in the complete models utilized in this work.

The small extent of $R$ where the artificial trilobite-like PEC becomes attractive can also be qualitatively understood in terms of the zero-range model. The atomic Rydberg states that are subjects of this study are relatively compact. Therefore, a small increase of the distance from the positive core yields a rapid decrease of $E_k^{(nl)}(R)$ (Fig. 9(b)). As a result of this mapping, the $e^-$-Rb interaction in the $s$-wave is attractive (and consequently induces attraction of the centers) in the narrow interval of distances from the positive core between the point corresponding to the Ramsauer minimum at $R_{\text{RM}} = 127$ a.u. and the classical turning point at 162 a.u. The interpretation the results beyond this point cannot be based on the local classical kinetic energy of the electron.

As can be seen in Fig. 9, the point where the artificial trilobite PEC changes its nature from the attractive to the repulsive (at $R \approx 135$ a.u.), does not accurately correspond to the Ramsauer minimum in the $3^3S^e$ $e^-$-Rb interaction. It is visible as the difference in $R$ and in $E_k$ marked by the magenta region. Since the difference of 8 a.u. is similar to the size of the ground-state Rb atom, this variation can be attributed to the effects of the atomic finite size. This is taken into account in the PECs calculated in this work while disregarded in the zero-range interpretation.

\section{VII. CONCLUSIONS}

The two-electron $R$-matrix method \cite{20} was applied to Rb$_2$ for a range of the internuclear separations between 35 a.u. and 200 a.u. in order to calculate the excited $3\Sigma^e$ electronic states of this LRRM. In addition to the interaction between the Rydberg electron and the neutral perturber considered also in the zero-range models of the LRRMs, this approach also takes into account the effect of the Coulomb potential due to the positive Rydberg core on the valence electron of the perturber.
Since this valence electron is explicitly represented, and its interaction with the Rydberg electron is treated as true Coulomb repulsion, it is equally accurate for a wide range of the interaction energies. This is different from the one-electron pseudopotential studies (see [21, 27] and references therein) where the interactions are optimized for a certain energy interval (typically around the zero kinetic energy).

The goal of the study presented in this article was to compare this complex two-electron approach with the simple zero-range model at the intermediate internuclear separations $R < 200$ a.u. where these can yield different energies. The PECs calculated using the two-electron $R$-matrix method showed similar overall character to those obtained from the zero-range model. The most notable differences appeared in the regions where the curves detach from the asymptotic energies of the degenerated hydrogen-like Rydberg states. The PECs attain ion-pair-like character near these points due to the low-energy $e^-$-Rb resonance and significant probability density of the Rydberg electron is localized in the vicinity of the perturber. It is not surprising that these states are sensitive to the details of all the interactions involving the perturber and they are accurately treated by the two-electron $R$-matrix technique.

The zero-range model [1, 5] and the two-electron approach also yield different results at small internuclear separations $R < 40$ a.u. This is due to the polarization of the perturber’s valence electron by the Coulomb tail of the potential due to the positively charged Rydberg atomic core and the discrepancies raise with decreasing distance between the nuclei.

The two-electron approach allowed for the calculation of the PECs associated with the excited state of the neutral perturber. The curves with the asymptotic energy of the state $5p + 4d$ were presented in this article. These electronic states involve energetically low and spatially compact states of the Rydberg electron. The PECs can be well approximated by the atomic energy of the perturber in the state $5p$ weakly polarized by the distant Rydberg core. The energy of the atomic Rydberg state $4d$ represents an additional constant shift (see Eq. (2)). This characteristics changes only at the low internuclear distances among those studied in this work.

The wave functions of the Rydberg electron were calculated using the one-electron model based on the finite-range potential representation of the perturber [16]. Since the obtained PECs qualitatively compare well to those calculated using the two-electron approach, it is reasonable to expect that the wave functions in both models have qualitatively similar character.

The perturbation of the non-degenerated atomic Rydberg states $ns$, $nd$ and $nf$ (with respect to the positive Rydberg center) by neutral Rb atom yields the bound states in agreement with the zero-range model [11, 5]. The wave functions retain their overall angular structure of the unperturbed atomic Rydberg states, the modification is localized in the vicinity of the perturber.

On the other hand, the global character of the perturbed atomic Rydberg states $np$ changes rapidly even while the perturber is distant from the Rydberg core and the wave functions show very complicated nodal structure involving high angular momenta. This is due to the fact that in Rb$_2$, at the internuclear separations studied in this work, the energies of the long-range molecular butterfly-like states involving high angular momenta with respect to the positive core are very close to the energy levels of the atomic Rydberg states $np$.

Another category of the molecular states involving high angular momenta of the Rydberg electron are the trilobite states. In the rage of the internuclear separations studied here, the PECs associated with these states are anti-bonding (monotonically decreasing with the internuclear distance) and they do not possess any vibrationally bound states. This is due to very small interval of $R$ where the classical energy of the Rydberg electron allows it to interact attractively with the rubidium perturber in the $s$-wave. Moreover, the $s$-wave attraction is too weak and the overall nature is dictated by the repulsive $p$-wave.

ACKNOWLEDGMENTS

The author is thankful to Roman Čurík for stimulating discussions of this research and for the critical reading of the manuscript. This work was supported by the Czech Science Foundation (Project No. P203/17-26751Y).

Appendix: Unphysical steeply raising PECs

Figs. 2 and 4 show, among other, three very steeply raising PECs that do not appear in the results provided by the zero-range model. They are artifacts of the computational approach to the matching of the wave functions on the $R$-matrix sphere. The steeply raising PECs correspond to the energies and internuclear separations at which the wave function inside the $R$-matrix sphere is matched to the trivial solution in the outer region that is represented by the Coulomb Green’s function along with the other, non-trivial, solutions. Although the correct asymptotic bound-state boundary conditions are satisfied in these cases, the zero wave function in the outer region enforced by the Coulomb Green’s function unphysically restricts the Rydberg electron to the region inside the $R$-matrix sphere. The small values of $\text{det}(M)$ at the energies near these unphysical states, where the matching matrix $M = \Gamma - \Gamma^{'} R$ (see TC Eq. (38)), are caused by small values of the elements in $\Gamma$ and $\Gamma^{'}$. These matrices only depend on the Coulomb Green’s function in the outer region and they are independent of the interaction between the Rydberg electron and the perturber (see TC Eqs. (37)) that is parametrized by the $R$-matrix. At the energies close to the unphysical points on the steep PECs, the matrices $\Gamma$ and $\Gamma^{'}$ are so small compared to
the matrix $\mathbf{R}$ that the interaction of the Rydberg electron with the perturber has very small influence on the position and shape of the unphysical steep PECs. Since these PECs are monotonic and they possess clear crossings with the other PECs, they can be easily distinguished from the physical PECs and they do not represent any complication for interpretation of the results.

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