

# Rydberg Quasimolecules Consisting of a Li-like Ion and a Fully-Stripped Ion: Classical Description of Crossings of Energy Terms and of Charge Exchange

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**ABSTRACT:** In year 2000 one of us published papers [1, 2] presenting a purely classical description of energy terms of Rydberg quasimolecules consisting of one electron and two fully-stripped ions of charges  $Z$  and  $Z'$ , where  $Z' \neq Z$ . The analysis of the crossings of the energy terms led to a classical description of charge exchange either between a hydrogen-like ion of the nuclear charge  $Z$  with a fully-stripped ion of the charge  $Z'$  or between a hydrogen-like ion of the nuclear charge  $Z'$  with a fully-stripped ion of the charge  $Z$ . These papers broke the paradigm, in which charge exchange was considered an inherently quantum phenomenon. Recently we extended the classical description of energy terms from one-electron Rydberg quasimolecules (hereafter, RQ1) to two-electron Rydberg quasimolecules (hereafter, RQ2) [21].

In the present paper we further extend the classical description of energy terms to *three-electron* Rydberg quasimolecules (RQ3), consisting of three electrons and two fully-stripped ions of charges  $Z$  and  $Z'$ . We show that classical energy terms of RQ3 also exhibit crossings like the energy terms of RQ1 and RQ2. The crossing of terms of RQ3 occurs at a larger internuclear distance compared to the crossing of the corresponding terms of RQ2, so that the cross-section of the charge exchange for RQ3 is larger than the corresponding cross-section for RQ2 (which in its turn is larger than for RQ1). Thus, the classical roots of charge exchange are revealed not only by the example of RQ1 and RQ2 systems, as in papers [1, 2, 21], but also by the examples of RQ3 systems.

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## 1. INTRODUCTION

In year 2000 one of us published papers [1, 2] presenting a purely classical description of energy terms of Rydberg quasimolecules consisting of one electron and two fully-stripped ions of charges  $Z$  and  $Z'$ , where  $Z' \neq Z$ . The analysis of the crossings of the energy terms led to a classical description of charge exchange either between a hydrogen-like ion of the nuclear charge  $Z$  with a fully-stripped ion of the charge  $Z'$  or between a hydrogen-like ion of the nuclear charge  $Z'$  with a fully-stripped ion of the charge  $Z$  [1, 2]. This meant that papers [1, 2] broke the paradigm, in which charge exchange was considered an inherently quantum phenomenon.

Later applications of these results were presented in papers [3-12] and summarized in review [13]. In papers [1, 3-7, 10, 11] the studies were focused at Circular Rydberg States (CRS) of the QR1 systems (the analysis in papers [2, 9, 12] went beyond CRS). CRS of atomic and molecular systems, with only one electron, correspond to  $|m| = (n - 1) \gg 1$ , where  $n$  and  $m$  are the principal and magnetic electronic quantum numbers, respectively. They have been extensively studied [14-17] both theoretically and experimentally for several reasons: (a) CRS have long radiative lifetimes and highly anisotropic collision cross sections, thereby enabling experiments on inhibited spontaneous emission and cold Rydberg gases [18, 19], (b) classical CRS correspond to quantal coherent states, objects of fundamental importance, and (c) a classical description of CRS is the primary term in the quantal method based on the  $1/n$ -expansion (see, e.g. [20] and references therein).

Recently we extended the classical description of energy terms from one-electron Rydberg quasimolecules (hereafter, RQ1) to two-electron Rydberg quasimolecules (hereafter, RQ2) [21]. In the present paper we further

extend the classical description of energy terms to *three-electron* Rydberg quasimolecules (RQ3), consisting of three electrons and two fully-stripped ions of charges  $Z$  and  $Z'$ . We show that classical energy terms of RQ3 also exhibit crossings like the energy terms of RQ1 and RQ2. The crossing of terms of RQ3 occurs at a larger internuclear distance compared to the crossing of the corresponding terms of RQ2, so that the cross-section of the charge exchange for RQ3 is larger than the corresponding cross-section for RQ2 (which in its turn is larger than for RQ1). Thus, the classical roots of charge exchange are revealed not only by the example of RQ1 and RQ2 systems, as in papers [1, 2, 21], but also by the examples of RQ3 systems.

## 2. ANALYTICAL CALCULATIONS OF CLASSICAL ENERGY TERMS

We consider a Rydberg quasimolecule formed by a Li-like ion of the nuclear charge  $Z$ , having two inner electrons in state  $1s$ , the highly excited outer electron in a circular state, and a fully stripped ion of the nuclear charge  $Z'$ . The outer electron is in the superposition of the Coulomb potential from charge  $Z'$  and the potential  $\Phi$  of a quasinucleus consisting of the nucleus  $Z$  and a spherically-symmetric charge distribution corresponding to the two inner electrons in the  $1s$  state (see, e.g., [22]):

$$\Phi(r) = \frac{Z-2}{r} + 2 \left( \left( Z - \frac{5}{16} \right) \mu + \frac{1}{r} \right) e^{-2 \left( Z - \frac{5}{16} \right) \mu r} \quad (1)$$

where  $\mu = Mm/(M+m)$  is the reduced mass of the pair “nucleus  $Z$ -electron”,  $M$  is the nuclear mass, and  $r$  is the radial coordinate. We use atomic units  $\hbar = e = m_e = 1$ .

The classical Hamilton function (for brevity, Hamiltonian) of the highly excited electron is

$$H = \frac{1}{2} \left( p_z^2 + p_\rho^2 + \frac{p_\phi^2}{\rho^2} \right) - \Phi(r) - \frac{Z'}{\sqrt{\rho^2 + (R-z)^2}} \quad (2)$$

where  $r = (\rho^2 + z^2)^{1/2}$  is the distance from the highly excited electron to the nucleus  $Z$  and  $(\rho, \phi, z)$  are the cylindrical coordinates, such chosen that the nuclei  $Z$  and  $Z'$  are on the  $z$ -axis at  $z = 0$  and  $z = R$ , respectively. Since the electron is in a circular state, then  $\phi$  is a cyclic coordinate and its corresponding momentum is conserved:

$$p_\phi = \rho^2 \frac{d\phi}{dt} = L \quad (3)$$

With (3) and (1) substituted into (2), we obtain

$$H = \frac{1}{2} (p_z^2 + p_\rho^2) + E \quad (4)$$

where

$$E = \frac{L^2}{2\rho^2} - \frac{Z-2}{\sqrt{\rho^2 + z^2}} - 2 \left( \left( Z - \frac{5}{16} \right) \mu + \frac{1}{\sqrt{\rho^2 + z^2}} \right) e^{-2 \left( Z - \frac{5}{16} \right) \mu \sqrt{\rho^2 + z^2}} - \frac{Z'}{\sqrt{\rho^2 + (R-z)^2}} \quad (5)$$

In a circular state,  $p_z = p_\rho = 0$ , and  $E$  becomes the total energy of the electron. Using the scaled quantities

$$\ell = \frac{L}{\sqrt{ZR}}, \quad w = \frac{z}{R}, \quad v = \frac{\rho}{R}, \quad p = v^2, \quad \varepsilon = -\frac{R}{Z} E, \quad k = \mu R, \quad b = \frac{Z'}{Z}, \quad r = \frac{Z}{L^2} R \quad (6)$$

we obtain the scaled energy  $\varepsilon$  of the electron

$$\varepsilon = \frac{1 - \frac{2}{Z}}{\sqrt{w^2 + p}} + \frac{b}{\sqrt{(1-w)^2 + p}} + \frac{2}{Z} \left( \left( Z - \frac{5}{16} \right) k + \frac{1}{\sqrt{w^2 + p}} \right) e^{-2 \left( Z - \frac{5}{16} \right) k \sqrt{w^2 + p}} - \frac{\ell^2}{2p} \quad (7)$$

From the equilibrium on the scaled coordinates ( $w$ ,  $p$ ) we require

$$\frac{\partial \varepsilon}{\partial w} = 0, \quad \frac{\partial \varepsilon}{\partial p} = 0 \quad (8)$$

The first out of the two derivatives in Eq. (8) being equated to zero yields the equilibrium relationship between the coordinates ( $w$ ,  $p$ ) for the given values of  $Z$ ,  $b$  and  $k$ . The explicit form of this relationship is:

$$\frac{b(1-w)}{\left( (1-w)^2 + p \right)^{3/2}} = \frac{1 - \frac{2}{Z}}{\left( w^2 + p \right)^{3/2}} + \frac{2}{Z} \frac{1 + 2 \left( Z - \frac{5}{16} \right) k \sqrt{w^2 + p} \left( 1 + \left( Z - \frac{5}{16} \right) k \sqrt{w^2 + p} \right)}{\left( w^2 + p \right)^{3/2}} e^{-2 \left( Z - \frac{5}{16} \right) k \sqrt{w^2 + p}} \quad (9)$$

Figure 1 shows an example plot  $p(w)$  for  $Z = 3$ ,  $b = 3$ ,  $k = 10$ .

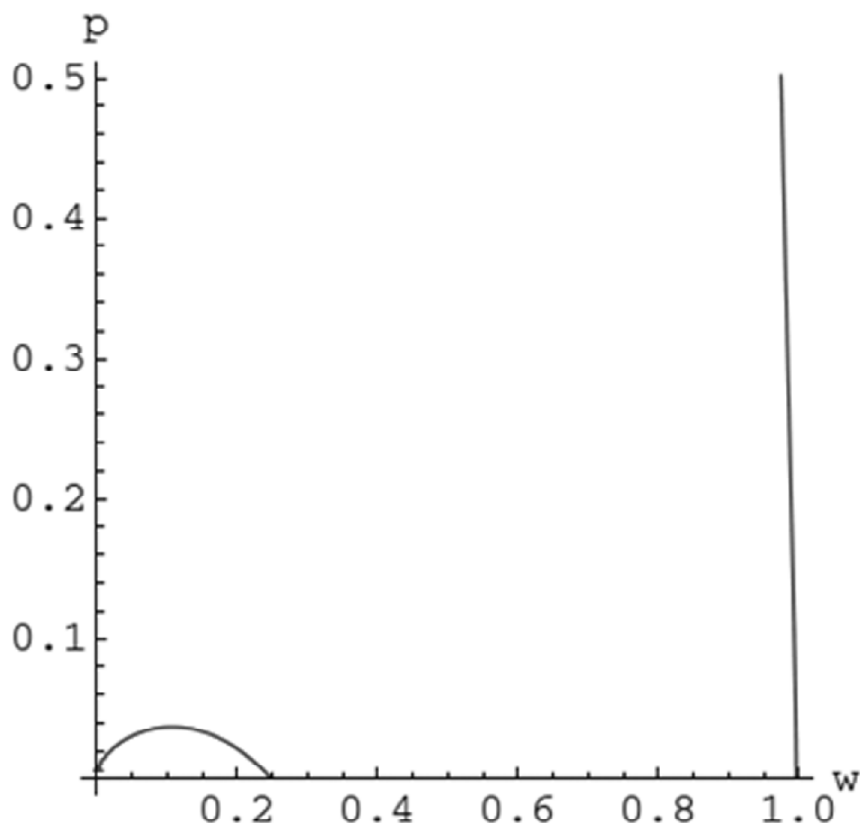


Figure 1: Equilibrium plot of the dependence of the squared scaled radius of the orbit  $p$  on the scaled axial coordinate  $w$  for  $Z = 3$ ,  $b = 3$ ,  $k = 10$ .

As in the case of RQ1 [1, 2], the equilibrium range is  $0 < w < w_1$  and  $w_3 < w < 1$ . In the present case,

$$w_1 = \frac{\alpha}{\left(Z - \frac{5}{16}\right)k} \quad (10)$$

where  $\alpha$  is the solution of the transcendental equation

$$\frac{2}{Z} + \frac{b\alpha^2}{\left(k\left(Z - \frac{5}{16}\right) - \alpha\right)^2} = 1 + \frac{2}{Z}\left(1 + 2\alpha + 2\alpha^2\right)e^{-2\alpha} \quad (11)$$

and the asymptote  $w = w_3$  is determined by

$$w_3 = \frac{b}{b + 1 - \frac{2}{Z}} \quad (12)$$

While calculating the second out of the two derivatives in Eq. (8), the last term in Eq. (7) survives. It contains the equilibrium value of  $\ell$ . We subtract the first derivative given by Eq. (9) from the second one and obtain the value of the scaled angular momentum in the circular state:

$$\ell^2 = \frac{bp^2}{w\left((1-w)^2 + p\right)^{3/2}} \quad (13)$$

From the scaling formulas of Eq. (6) it follows that  $r = 1/\ell^2$ , that is,

$$r = \frac{w\left((1-w)^2 + p\right)^{3/2}}{bp^2} \quad (14)$$

Substituting Eq. (13) into Eq. (7), we obtain the scaled energy:

$$\varepsilon = \frac{1 - \frac{2}{Z}}{\sqrt{w^2 + p}} + b \frac{(1-w)^2 + p \left(1 - \frac{1}{2w}\right)}{\left((1-w)^2 + p\right)^{3/2}} + \frac{2}{Z} \left( \left(Z - \frac{5}{16}\right)k + \frac{1}{\sqrt{w^2 + p}} \right) e^{-2\left(Z - \frac{5}{16}\right)k\sqrt{w^2 + p}} \quad (15)$$

From Eq. (6),  $k = \mu R$ , where  $\mu$  is the reduced mass of the pair nucleus–electron. In our units, the mass of the electron is 1, so  $\mu = M/(1 + M)$ , where  $M$  is the nuclear mass  $Zm_p + Nm_n$  of the nucleus containing  $Z$  protons and  $N$  neutrons. In atomic units,  $m_p \approx 1849.3596$  and  $m_n \approx 1851.9088$ . Since

$$\mu = \frac{M}{1 + M} = \frac{1}{\frac{1}{M} + 1} = \frac{1}{\frac{1}{Zm_p + Nm_n} + 1} \approx \frac{1}{\frac{1}{(Z + N)m_p} + 1} \quad (16)$$

the lower limit of  $\mu$  is realized when  $Z = 1$  and  $N = 0$  and is approximately 0.99946 and the upper limit is 1. Therefore, the realistic values of  $\mu$  lie in the range  $0.99946 \leq \mu < 1$ . The values of  $R$  for the case of a Rydberg

quasimolecule are of the order of several Bohr radii. Thus, the realistic values of  $k = \mu R$  are in the range from 1 or 10. Physically,  $k$  represents the slightly scaled internuclear distance.

The last term in Eq. (9) containing the exponential function is small and can be neglected, enabling the possibility of an analytical solution. This equation can then be solved for  $p$ , which can then be substituted into Eqs. (15) and (14), thus yielding the equilibrium equations for  $\varepsilon$  and  $r$ . Also, from the scaling formulas we see that  $E = -(Z/L)^2 \varepsilon/r$ , so if we denote  $\varepsilon/r = \varepsilon_1$ , then  $\varepsilon_1$  and  $r$  will have the same scaling. Thus, we obtain the parametric dependence  $\varepsilon_1(r)$  for the given  $b$ ,  $r$ ,  $Z$ ,  $L$ ,  $N$  with the parameter  $w$  taking all values in the allowed range  $0 < w < w_1$ ,  $w_3 < w < 1$ , where  $w_1$  is given by the approximate value

$$w_1 \approx \frac{1}{1 + \sqrt{\frac{b}{1 - \frac{2}{Z}}}} \quad (17)$$

and  $w_3$  is given by Eq. (12). This dependence can be simplified further by introducing the parameter [13]

$$\gamma = \left( \frac{1}{w} - 1 \right)^{1/3} \quad (18)$$

The final approximate analytical parametric dependence is as follows:

$$\varepsilon_1 = \left( 1 - \frac{2}{Z} \right) \frac{\gamma (c^{2/3} - \gamma^4)^2}{\gamma^6 - 1} \left( \left( 1 - \frac{2}{Z} \right) \frac{\gamma (\gamma^3 - 2) + c^{2/3} (2\gamma^3 - 1)}{2\gamma (\gamma^3 - 1)^2} + \frac{2}{Z} \right) \left( \frac{1}{\gamma^3 - 1} + \mu L^2 \frac{\left( 1 - \frac{5}{16Z} \right) (\gamma^6 - 1)}{\left( 1 - \frac{2}{Z} \right) (c^{2/3} - \gamma^4)^2} \right) e^{-2\mu L^2 \frac{\left( 1 - \frac{5}{16Z} \right) (\gamma^6 - 1)^2}{1 - \frac{2}{Z} \gamma (\gamma^3 + 1) (c^{2/3} - \gamma^4)^2}} \quad (19)$$

$$r = \frac{1}{\left( 1 - \frac{2}{Z} \right)} \frac{(\gamma^6 - 1) \sqrt{c^{2/3} \gamma^2 - 1}}{\gamma (c^{2/3} - \gamma^4)^2} \quad (20)$$

where

$$c = \frac{b}{1 - \frac{2}{Z}} \quad (21)$$

and the parameter  $\gamma$  takes all values in the allowed range  $0 < \gamma < 1/c^{1/3}$ ,  $c^{1/6} < \gamma < +\infty$ .

Figures 2 and 3 present the classical energy terms  $\varepsilon_1(r)$  for RQ3 for the case  $b = 3$ ,  $Z = 6$ ,  $N = 6$ ,  $L = 10$  in comparison with those of the RQ1 (Fig. 2) or RQ2 (Fig. 3), both of the latter shown in thinner curves.

We also performed an exact numerical solution to this problem. From the scaling formula for  $R$ ,  $k = (\mu L^2/Z)r$  with  $\mu$  given by Eq. (16). Equation (14), after being squared, is a fourth-degree polynomial with respect to  $p$  and has a real positive analytical solution for  $p$  which depends on  $r$ :  $p_0 = p(w, b, r)$ . Substituting  $k$  and the solution for  $p$  into

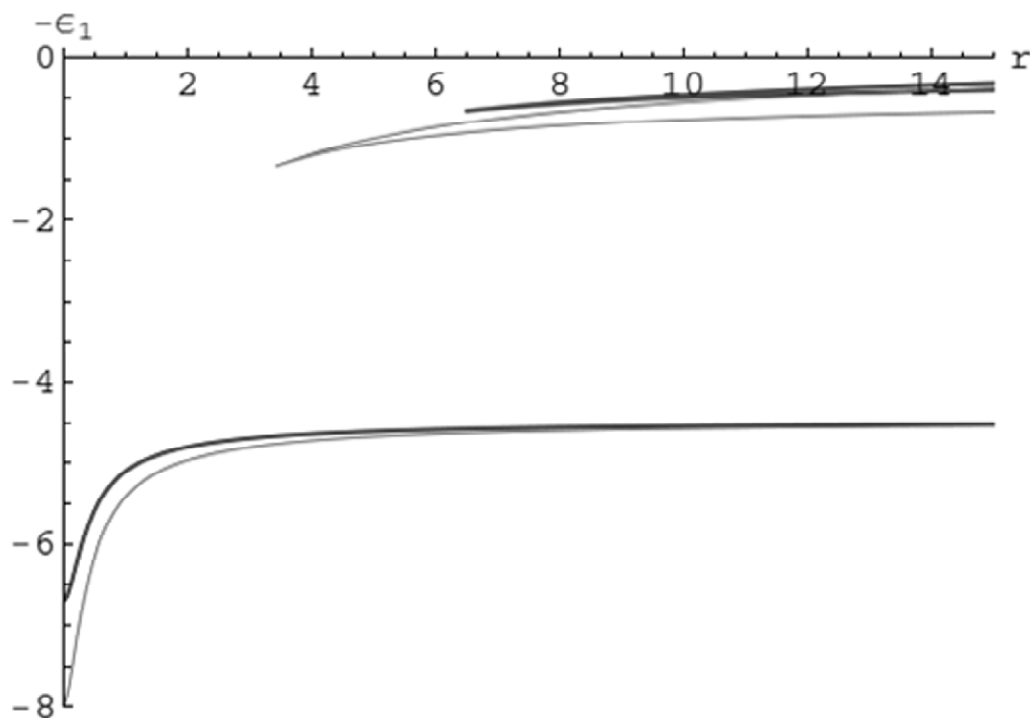


Figure 2: Classical energy terms  $\epsilon_1(r)$  for the case of RQ3 for  $b = 3$ ,  $Z = 6$ ,  $N = 6$ ,  $L = 10$  (thick curve) and the corresponding terms for the case of RQ1 (thin curve). RQ1 and RQ3 stand for Rydberg quasimolecules with 1 or 3 electrons, respectively.

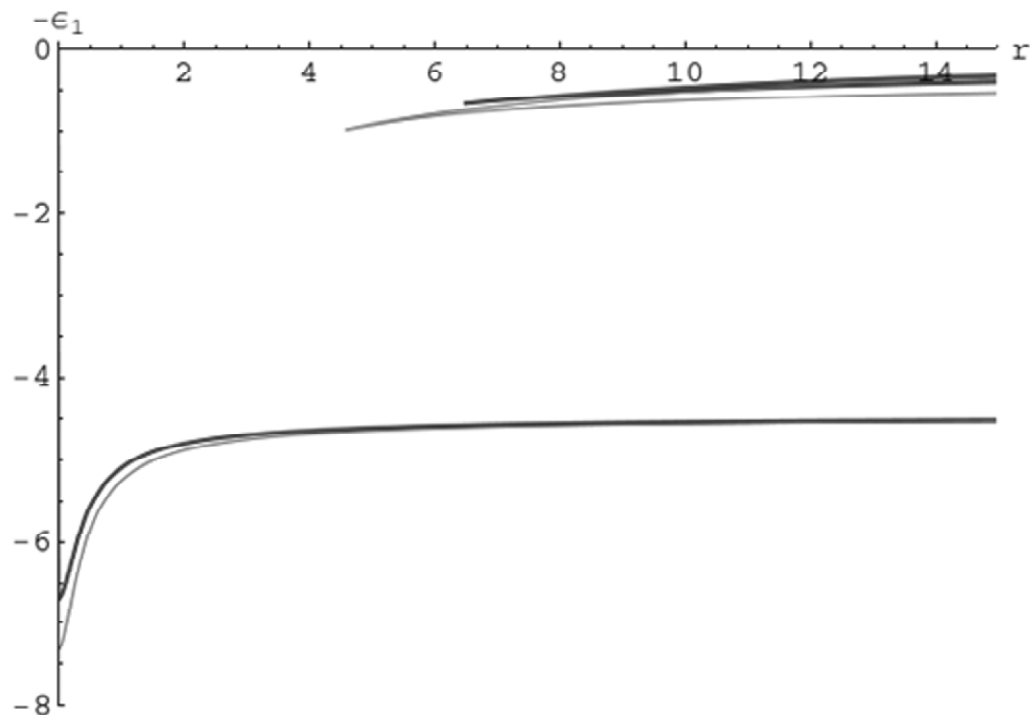


Figure 3: Classical energy terms  $\epsilon_1(r)$  for the case of RQ3 for  $b = 3$ ,  $Z = 6$ ,  $N = 6$ ,  $L = 10$  (thick curve) and the corresponding terms for the case of RQ2 (thin curve). RQ2 and RQ3 stand for Rydberg quasimolecules with 2 or 3 electrons, respectively.

Eqs. (15) and (9), we obtain the formula for energy  $\varepsilon(w, b, r, Z, L, N)$  and Eq. (9) bearing the same variables. Then we solve the resulting Eq. (9) for  $w$  (it may have up to 3 solutions) and substitute them into  $\varepsilon(w, b, r, Z, L, N)$ . Also, from the scaling formulas we see that  $E = - (Z/L)^2 \varepsilon/r$ , so if we denote  $\varepsilon/r = \varepsilon_1$ , then  $\varepsilon_1$  and  $r$  will have the same scaling. Thus, we obtain the energy  $\varepsilon_1(b, r, Z, L, N)$ , which yields the classical energy terms  $\varepsilon_1(r)$  for the given values of  $b, Z, L$  and  $N$ . The exact plot of the classical energy terms in the above example is visually indistinguishable from the approximate analytical ones. The analysis of the absolute error between the approximate and exact values for  $p$  and  $r$  shows a vanishingly small error (less than  $10^{-10}$ ) in almost all cases considered.

### 3. RELATION TO CHARGE EXCHANGE

When  $Z_{\text{eff}} = Z - 2$  and  $Z'$  differ significantly from each other, the V-type crossings occur between two classical energy terms that can be asymptotically labeled as  $Z_{\text{eff}}$ - and  $Z'$ -terms. This situation *classically depicts charge exchange*, as explained in papers [1, 2]. Indeed, say, initially at  $r \rightarrow \infty$ , the electron was a part of the ion of the nuclear charge  $Z_{\text{min}} = \min(Z', Z_{\text{eff}})$ . As the charges  $Z_{\text{eff}}$  and  $Z'$  come relatively close to each other, the two terms undergo a V-type crossing and the electron is shared between the  $Z_{\text{eff}}$ - and  $Z'$ -centers. Finally, as the charges  $Z_{\text{eff}}$  and  $Z'$  go away from each other, the electron ends up as a part of the ion of the nuclear charge  $Z_{\text{max}} = \max(Z', Z_{\text{eff}})$ .

From Fig. 2 it is seen that the V-type crossing of the upper two terms for RQ3 occurs at a larger internuclear distance than for RQ1. Therefore the cross-section of the charge exchange for RQ3 is larger than the corresponding cross-section for RQ1.

From Fig. 3 it is seen that the V-type crossing of the upper two terms for RQ3 occurs at an even larger internuclear distance than for RQ2. Therefore the cross-section of the charge exchange for RQ3 is even larger than the corresponding cross-section for RQ2.

### 4. CONCLUSIONS

We extended the classical description of energy terms from one-electron Rydberg quasimolecules (RQ1) and two-electron Rydberg quasimolecules (RQ2) to *three-electron* Rydberg quasimolecules (RQ3). We obtained the classical energy terms of RQ3, and found that they exhibit crossings like the energy terms of RQ1 and RQ2.

We explained the relation between the crossings of the classical energy terms and charge exchange. Thus, the classical roots of charge exchange have been revealed not only by the example of RQ1 and RQ2 systems, as in papers [1, 2, 21], but also by the example of RQ3 systems.

The crossing of terms of RQ3 occurs at an even larger internuclear distance compared to the crossing of the corresponding terms of RQ2, so that the cross-section of the charge exchange for RQ3 is even larger than the corresponding cross-section for RQ2 (which in its turn is larger than for RQ1).

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