Modification of molecular Rydberg states by superpromotion of the diabatic term to the continuous spectrum

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A study is made of the electron component of the adiabatic wave function of a molecular Rydberg state in the specific case of two Coulomb centers. An analytic expression for the quantum defect is obtained by the standard-equation method and the effect of modification of Rydberg states associated with superpromotion of the diabatic term is considered.

1. INTRODUCTION

Molecular Rydberg states are being investigated intensively both by experimental and theoretical methods (see, for example, Ref. 1 and the bibliography given there). A theory of molecular Rydberg states is considerably more complex than that of atomic states. Difficulties are encountered already in the solution of the problem of classification of the states, i.e., in introduction of a complet set of quantum numbers. Currently the most highly developed is the method of the multichannel quantum defect in which the wave function of a molecule can be represented by a superposition of states obtained by adiabatic separation of the electronic, vibrational, and rotational degrees of freedom.

We shall consider the most complex (electronic) part of the adiabatic wave function of a Rydberg state in the specific case of two Coulomb centers. This system has specific features of a diatomic molecule and is fairly simple to analyze, but its Rydberg states have not yet been investigated. We shall use the standard-equation method to obtain analytic expressions for the quantum defect and we shall study the influence of modification of Rydberg states because of superpromotion to the continuous spectrum of a diabatic term discovered in Ref. 2. Such a modification affects the majority of states; it is not related to the one-electron nature of the system under consideration and it should play an important role in the general theory of molecular Rydberg states.

The Schrödinger equation for the problem of two Coulomb centers can be modified by separating the variables in terms of prolate spheroidal coordinates ξ, η, φ ($1 \leqslant \xi < \infty$, $-1 \leqslant \eta \leqslant 1$, $0 \leqslant \varphi < 2\pi$) and, on substitution of the electron wave function in the form

$$\psi(\mathbf{r}) = [(\xi^2-1)(1-\eta^2)]^{-1/2} F(\xi)\Phi(\eta) e^{im\varphi}$$

reduces to the following system of equations[3] ($\hbar = m_e = e = 1$):

$$\frac{d^2F}{d\xi^2} + \left[-p^2 + \frac{a\xi-\lambda}{\xi^2-1} + \frac{1-m^2}{(\xi^2-1)^2}\right] F = 0, \qquad (1)$$

$$\frac{d^2\Phi}{d\eta^2} + \left[-p^2 + \frac{b\eta+\lambda}{1-\eta^2} + \frac{1-m^2}{(1-\eta^2)^2}\right] \Phi = 0, \qquad (2)$$

$$p = (-2E)^{1/2}R/2, \quad a = (Z_1+Z_2)R, \quad b = (Z_2-Z_1)R,$$

where E is the energy of an electron in the field of two Coulomb centers with charges Z_1 and Z_2 (adiabatic term); R is the intracenter (internuclear) distance. The terms $E(R)$ will be classified using spherical quantum numbers n, l, and m of a combined hydrogen-like atom with energy levels to which the adiabatic terms of the system reduce in the limit $R = 0$ (in the case of finite values of R the square of the total angular momentum of an electron is obviously not conserved and l is simply one of the indices labeling the states).

Rydberg states have low values of the energy or, in terms of Eqs. (1) and (2), low values of the parameter p. Near the limit of the continuous spectrum the terms of such a system can be represented in the form

$$E_{nlm}(R) = -Z^2/2[n+\Delta_{lm}(R)]^2 + O(n^{-4}), \qquad (3)$$

where $Z = Z_1 + Z_2$; $\Delta_{lm}(R)$ is a quantity which is independent of the principal quantum number n and which—by analogy with the theory of atoms—we shall call the quantum defect. The aim of our theoretical treatment will be to calculate the function $\Delta_{lm}(R)$.

Before actual calculations of the quantum defect, we must mention one qualitative features of the terms in the problem of two Coulomb centers, which plays an important role in our discussion. A numerical calculation of the terms in the problem of two Coulomb centers in a complex plane R revealed[2] diabatic terms $W_{lm}(R)$ which are promoted to the continuous spectrum. Promotion of a term $W_{lm}(R)$ to the continuous spectrum has the effect that all the adiabatic terms with a given set of quantum numbers $\{l,m\}$ experience consecutive quasicrossing of levels, giving rise to the familiar minima at terms with $l > \sqrt{3}m$. This effect is called the superpromotion in Ref. 4. For $m = 0$ the points of promotion of diabatic terms to the continuous spectrum can be estimated approximately[2] using the expression $R_{lm} = (l+\frac{1}{2})^2/Z$ and in the vicinity of such points the adiabatic terms of a given $\{l,m\}$ series change greatly. This effect is explained in Ref. 2 by a modification of the states from a one-center geometry for $R < R_{lm}$ to a two-center geometry for $R > R_{lm}$. Such a modification should be retained also in the limit $n \to \infty$ and should result in a specific behavior of the quantum defect in the vicinity of the point R_{lm}.

2. QUANTUM DEFECT IN THE PROBLEM OF TWO COULOMB CENTERS

We shall obtain approximately expressions for the quantum defect and study modification of Rydberg states

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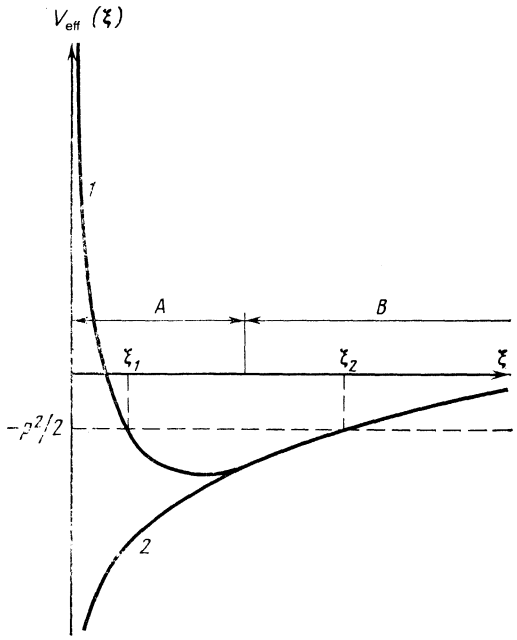

FIG. 1. Effective potential for the radial equation (1): 1) $a<\lambda$; 2) $a>\lambda$.

caused by superpromotion of a term $W_{lm}(R)$ by the standard-equation method in which we shall consider a and λ as large parameters of the same order of magnitude. We shall assume that $m=O(1)$ and $p\to 0$. This separation of large parameters distinguishes the present approach from the approximation of a combined atom ($a\to 0, p\to 0$) and from the approximation of separate atoms ($a\to\infty, p\to\infty$).

We shall first consider the symmetric case when $Z_1=Z_2$. Then, $b=0$ and in the limit $p\to 0$ the dependence on R disappears from the angular equation (2). Using the conventional standard equation method with the large parameters selected as above, we find that the separation constant is

$$\lambda=(l+{}^1/_2)^2. \tag{4}$$

The problem then reduces to a study of just the radial equation (1), where λ is described by Eq. (4). The effective potential for the radial equation contains not only the Coulomb interaction and the centrifugal interaction proportional to λ, but also an interaction proportional to m^2-1, which can be ignored in the first approximation, and the singularity of this interaction at $\xi=1$ (a second-order pole) is allowed automatically by choosing a standard equation which has the same singularity. Consequently, in the first approximation, the effective potential is

$$V_{\text{eff}}(\xi)=\frac{\lambda-a\xi}{2(\xi^2-1)}=\frac{\lambda-a}{4(\xi-1)}-\frac{\lambda+a}{4(\xi+1)}. \tag{5}$$

Equation (5) has a Coulomb singularity at $\xi=1$ and its important feature is a reversal of the sign of the effective charge $q=(\lambda-a)/4$ at $\lambda=a$, i.e., at $R=R_{lm}$. The reason for reversal of the sign of q can be explained as follows. In the case of a classical Coulomb path of an electron of zero energy with an angular momentum $l+\frac{1}{2}$ the distance of the closest approach to a charge Z is[5] $r_{\min}=(l+\frac{1}{2})^2/2Z$. Such a path corresponds to the limit of a combined atom and describes approximately the motion of an electron in the case of low values of R. If the focus of the path is located at the geometric center of the nuclei, then at low values of R the electron does not reach the nuclei and this is manifested by centrifugal repulsion at low values of $\xi-1$ in the effective radial potential (curve 1 in Fig. 1). If $R\geqslant 2r_{\min}=R_{lm}$ the path may cross the nuclei so that the effective potential (5) is qualitatively similar to the effective radial Coulomb potential for an s state in the spherically symmetric case (curve 2 in Fig. 1). Reversal of the sign of q is accompanied by a change in the quasiclassical boundary condition in the region of $\xi\approx 1$, which in the final analysis results in superpromotion of a diabatic term $W_{lm}(R)$ to the continuous spectrum.

A uniform asymptote valid in the vicinity of the point R_{lm}, where the effective charge q changes its sign, can be obtained by dividing the whole interval of ξ into two regions (Fig. 1). In the region denoted by A the standard equation is the Whittaker equation

$$\frac{d^2y}{d\xi^2}+\left[k^2-\frac{2q}{\xi-1}+\frac{1-m^2}{4(\xi-1)^2}\right]y=0, \tag{6}$$

which allows simultaneously for the singularity at $\xi=1$ and for a turning point ξ_1. In the region B we can use the conventional quasiclassical asymptote $F(\xi)$, which is uniform at a second turning point ξ_2 and decreases in the limit $\xi\to\infty$. Allowing the usual procedure in the standard-equation method,[3,6] we obtain the quantization condition

$$\int_{\xi'}^{\xi_2}\left(\frac{a\xi-\lambda}{\xi^2-1}-p^2\right)^{1/2}d\xi=\pi\left(n_r-\frac{1}{4}\right)+\delta(\gamma), \tag{7}$$

where $n_r=1,2,3,\ldots$ is the radial quantum number; $\xi'=1$ when $a>\lambda$ and $\xi'=\xi_1$ when $a<\lambda$; $\gamma=q/k$;

$$\delta(\gamma)=\frac{m-1}{4}\pi-\gamma(1-\ln|\gamma|)-\frac{1}{2}\ln\left[\Gamma\left(\frac{m+1}{2}+i\gamma\right)\Big/\Gamma\left(\frac{m+1}{2}-i\gamma\right)\right]$$

is the phase shift of the solution of Eq. (7) which is regular at $\xi=1$. The value of γ is found from the condition

$$\gamma=\frac{1}{\pi}\int_1^{\xi_1}\left(p^2-\frac{a\xi-\lambda}{\xi^2-1}\right)^{1/2}d\xi, \tag{8}$$

which ensures that the turning point ξ_1 in Eq. (1) is the same as that in the standard equation (6). The quantization condition (7) is the starting point in the calculation of the quantum defect. In general, this condition represents a transcendental equation for the energy, but in the limit $p\to 0$ it can be solved explicitly. Consequently, using the relationship between the quantum numbers $n=n_r+l$ and going to the limit $n\to\infty$ and $n_r\to\infty$, we find that the quantum defect $[\Delta_{lm}(R)=\tilde{\Delta}_{lm}(R)+O(\lambda^{-1/2})]$ is described by

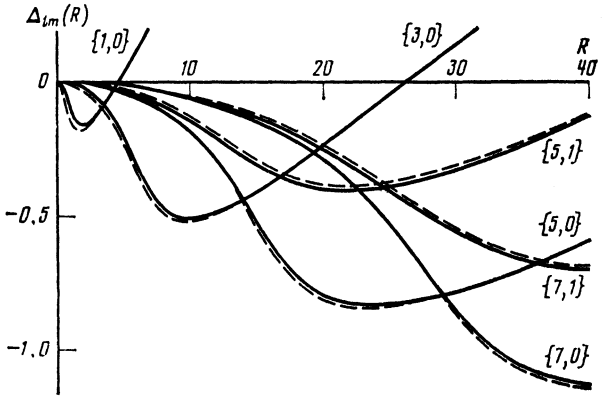

FIG. 2. Exact (continuous curves) and calculated from Eq. (9) (dashed curves) values of the quantum defect for H_2^+. The curly brackets along the curves give the values of the quantum numbers l and m.

$$\tilde{\Delta}_{lm}(R)=\frac{m}{4}-\frac{1}{2}-l-\frac{1}{2\pi}\times\ln\left[\Gamma\left(\frac{m+1}{2}+i\gamma\right)\Big/\Gamma\left(\frac{m+1}{2}-i\gamma\right)\right]-\frac{\gamma}{\pi}+\begin{cases}\frac{1}{\pi}\gamma\ln(-\gamma)\\ +\frac{1}{\pi}(2a)^{1/2}\left[2E\left(\frac{\lambda+a}{2a}\right)-\left(1-\frac{\lambda}{a}\right)K\left(\frac{\lambda+a}{2a}\right)\right], & a\geqslant\lambda\\ \frac{1}{\pi}\gamma\ln\gamma+\frac{1}{\pi}2(a+\lambda)^{1/2}E\left(\frac{2a}{a+\lambda}\right), & a\leqslant\lambda,\end{cases}\qquad(9)$$

where $K(z)$ and $E(z)$ are complete elliptic integrals of the first and second kind, defined in accordance with Ref. 7. The value of γ in Eq. (8) is in this limit given by

$$\gamma=\frac{1}{\pi}(2a)^{1/2}\left[\left(1+\frac{\lambda}{a}\right)K\left(\frac{a-\lambda}{2a}\right)-2E\left(\frac{a-\lambda}{2a}\right)\right],\quad a\geqslant\lambda,$$
$$\gamma=2\frac{1}{\pi}(a+\lambda)^{1/2}\left[K\left(\frac{\lambda-a}{\lambda+a}\right)-E\left(\frac{\lambda-a}{\lambda+a}\right)\right],\quad a\leqslant\lambda.\qquad(10)$$

At first sight it seems that Eqs. (9) and (10) are different in the ranges $a>\lambda$ and $a<\lambda$, but we an easily show (using the properties of complete elliptic integrals) that the two variants are analytic continuations of each other. We have written Eqs. (9) and (10) in this form so that in each of the intervals $a>\lambda$ and $a<\lambda$ the arguments of the functions $K(z)$ and $E(z)$ lie within the standard interval $0\leqslant z<1$.

In the limit of a combined atom the quantum defect $\tilde{\Delta}_{lm}(R)$ vanishes, which is identical with the exact value of this defect when $R=0$. At the point $a=\lambda$, where q changes its sign, we have $\tilde{\Delta}_{lm}=(2^{3/2}/\pi-1)(l+1/2)$. At high values of R ($a\gg\lambda$) Eq. (9) simplifies and in the first approximation it becomes

$$\tilde{\Delta}_{lm}(R)=2\Gamma^{-2}\left(\frac{1}{4}\right)(2\pi ZR)^{1/2}-l+\frac{m-1}{2}+O(R^{-1/2}).\qquad(11)$$

Figure 2 shows, for comparison, the values calculated using Eq. (9) and the exact values of the quantum defect. These exact values of $\Delta_{lm}(R)$ were obtained by extrapolation of the exact adiabatic terms with $n_r\leqslant 10$ to the limit of the continuous spectrum. We can see from Fig. 2 that the agreement is good even in the case of low values of l. The major change in the quantum defect in the region of $R\approx R_{lm}$ represents quasicrossing of terms which in this case is due to promotion (via Rydberg densification of levels) of a diabatic term $W_{lm}(R)$ to the continuous spectrum.

3. SUPERPROMOTION OF A DIABATIC TERM $W_{lm}(R)$

The analytic expression (9) can be used to calculate sufficiently accurately the terms of highly excited states in the problem of two Coulomb centers. Nevertheless, it is important to note that in rigorous numerical calculations an increase in n requires a much greater computer time and for $n_r>10$ such calculations become practically impossible. However, an even more important result is the explicit separation in Eq. (9) of a logarithmic singularity associated with superpromotion of a term $W_{lm}(R)$. The usual quasicrossing of a pair of adiabatic terms is associated with a common root branching point.[9] This situation differs from the conventional case because superpromotion of a diabatic term $W_{lm}(R)$ creates an infinite chain of level quasicrossings. The corresponding branching points $\mathscr{R}_{nlm}$ form in turn an infinite series of points which are localized in a small region on a complex plane R and which become more closely spaced approaching a certain limiting point $\mathscr{R}_{lm}$ when $n\to\infty$. In the first approximation such a series is equivalent to a logarithmic branching point.[2]

Equation (9) has logarithmic branching points in the complex plane R where the argument of the Γ function vanishes:

$$(m+1)/2\pm i\gamma(R)=0.\qquad(12)$$

A preliminary analysis shows that solutions of Eq. (12) are located in the region where $|\lambda-a|/|\lambda+a|\ll 1$, so that in the definition of the function $\gamma(R)$ given by Eq. (10) we can expand complete elliptic integrals as Taylor series. Retaining in $\gamma(R)$ the first two terms of the expansion, we obtain from Eq. (12) two complex-conjugate values of a logarith-

TABLE I. Exact $\mathscr{R}_{lm}$ and calculated from Eq. (13) approximate $\tilde{\mathscr{R}}_{lm}$ logarithmic branching points in complex plane of internuclear distance R.

$\{l, m\}$	{1,0}	{3,0}	{5,0}	{7,0}	{5,1}	{7,1}
Re $\tilde{\mathscr{R}}_{lm}$	0.87	5.9	14.9	27.9	14.1	27.1
Re $\mathscr{R}_{lm}$	0.75	5.8	14.8	27.8	13.4	26.7
Im $\tilde{\mathscr{R}}_{lm}$	1.03	2.5	3.9	5.3	7.7	10.6
Im $\mathscr{R}_{lm}$	1.02	2.5	3.9	5.3	7.6	10.5

mic branching point:

$$\tilde{\mathscr{R}}_{lm}=\{(l+1/2)^2-1/2(m+1)^2$$
$$\pm i(m+1)[2(l+1/2)^2-1/4(m+1)^2]^{1/2}\}/Z. \quad (13)$$

Table I gives the values of $\tilde{\mathscr{R}}_{lm}$ from Eq. (13) and the exact numerical values of logarithmic limiting points of the $\mathscr{R}_{lm}$ type for several $\{lm\}$ series. We can see from Table I that $\mathscr{R}_{lm}$ can be calculated reliably using the simple formula (13).

Knowledge of the complex quantity $\mathscr{R}_{lm}$ is of major practical importance. It is needed in the theory of atomic collisions when calculations are made of cross sections of nonadiabatic transitions caused by the interaction between a diabatic term $W_{lm}(R)$ with an infinite Rydberg series of levels[2]: the real part of $\mathscr{R}_{lm}$ determines the range of impact parameters for which such transitions take place, whereas the imaginary part determines the probability of transitions (Massey criterion).

The logarithmic branching point $\tilde{\mathscr{R}}_{lm}$ relates the adiabatic terms of a given $\{lm\}$ series so that they form a single analytic function $E_{lm}(R)$. We can see from Eq. (9) that a single trip around a point $\tilde{\mathscr{R}}_{lm}$ changes the value of $\tilde{\Delta}_{lm}(R)$ by unity, which corresponds to a transition in Eq. (3) from the initial term $E_{nlm}(R)$ to the next term $E_{n\pm 1lm}(R)$ (the sign $\pm$ is governed by the direction of the trip). The principal quantum number n then acts as the quantum number of a sheet of a multisheet analytic function $E_{lm}(R)$.

4. CONCLUSIONS

If $Z_1 = Z_2$, Eq. (9) for the quantum defect is not affected and the only change is in the separation constant λ, found from the angular equation (2). Then, instead of Eq. (4), we can use the approximate expression[3]

$$\lambda=(l+1/2)^2-b^2/8(l+1/2)^2, \quad (14)$$

which is valid when $0<R<(l+1/2)^2/|Z_1-Z_2|$, and which includes the region $R\approx R_{lm}$ where the modification takes place. In the modification region the values of λ of Eqs. (4) and (14) differ little from one another and the role of the charges Z_1 and Z_2 reduces mainly to a change in the scale in the complex plane of the internuclear distance: $\tilde{\Delta}_{lm}=\tilde{\Delta}_{lm}(ZR)$.

Real Rydberg states do have large but finite values of the principal quantum number n, so that they are characterized by three qualitatively different ranges of R governed by the size of an electron cloud $r_{av}\approx[3n^2-l(l+1)]/2Z$: a quasimolecular region $0\leqslant R\leqslant r_{av}$, a region of separate atoms $r_{av}\ll R<\infty$, and a transition region $R\approx r_{av}$. These results are valid only in the quasimolecular range.

It follows from the above analysis that the nature of the electronic part of the total wave function of a molecular Rydberg state and the magnitude of the quantum defect depend strongly on the ratio of the internuclear distance and the effective impact parameter of an electron (i.e., λ and R) in the region of $R\approx R_{lm}$. This effect is accompanied by a strong interaction between adiabatic states, which results in tangling (crossing) of a large number of such states in the total wave function of the molecule at $R\approx R_{lm}$.

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