Rydberg states of molecules

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A generalized version of the multichannel quantum defect (MQD) theory is proposed for the investigation of the Rydberg states of molecules. The basic equations of the MDQ theory are derived under fairly general assumptions regarding the nature of the interaction between the electron and the ion core. If the adiabatic reaction matrix or the reaction parameters are known, the obtained equations allow the determination of the structure of the electron spectrum under conditions when the period of the electron motion is comparable to the period of the vibrational or rotational motion of the molecule and the energy levels are characterized by a significant irregularity in their disposition. The equations of the theory are analyzed for molecules of the symmetrical-top type (without allowance for the combined effect of the vibrational and rotational motions on the Rydberg states of the electron). The autoionization level widths of molecular hydrogen are determined, and the theory is compared with the experimental data and versions of the simplified theory.

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1. INTRODUCTION

The highly excited Rydberg states of molecules have been the subject in recent years of intensive experimental and theoretical study,[1-14] which is explained by the important role played by these states in the processes of photoionization and ionization of molecules during collisions with electrons. If one of the electrons of the atom or molecule is in a highly excited state, its energy spectrum has the hydrogenic-level structure:

$$E_n=-1/2(n-\mu_s)^2, \qquad (1)$$

where μ_s is the Rydberg level shift and s is the set of quantum numbers specifying the system with allowance for the internal degrees of freedom (here and below we use the atomic system of units with $\hbar=m_e=e=1$). The quantum defect (QD) theory has been widely used to investigate states of this type.[15-19]

The problem before the QD theory is the determination of the quantities μ_s or their connection with parameters observed in other physical processes (e.g., in electron scattering by atomic and molecular ions[20,21], etc.). For atoms, this problem has been investigated fairly thoroughly.

The quantum defect in Rydberg states of molecules is found to depend not only on the orbital motion of the electron and the state of the ion core M^+, but also on the principal quantum number n.[1-4] The dependence on n is due to the change in the character of the coupling between the electronic and nuclear motions as the binding energy of the electron decreases. For small n, when the electronic-level spacing, $1/n^3$, is significantly greater than the vibrational and rotational energy quanta (i.e., when $1/n^3 \gg B, \omega$), the motion is adiabatic, and the Rydberg shifts are determined by the quantization rules for the motion of an electron in the field of a stationary molecule. In this case the energy levels are correctly given by the formula (1), with μ_s parametrically depending on the set of vibrational coordinates, ξ, of the molecular ion M^+. As n increases, the adiabatic coupling between the electron and the vibrational (when $1/n^3 \sim \omega$) and then the rotational (when $1/n^3 \sim B$) motions is severed, i, e., there occurs a significant restructuring of the electronic spectrum. The study of this effect on the basis of information obtained in the adiabatic approximation is the main problem of the multichannel quantum defect (MQD) theory. At present this theory has been developed only for the simplest molecules (of the type H_2).[2,8,12] In its original formulation, given by Fano,[8] the MQD theory allows for only a two-channel nonadiabatic coupling with the rotational motion, since the effect of the nonadiabatic electron-vibrational motion coupling for the unexcited core can be neglected because of the presence of a small parameter (the ratio of the vibration amplitude to the interatomic distance). But in view of the recently increased requirements for optical diagnostics of vibrationally excited molecules, it is necessary to have a MQD theory that takes into consideration the combined effect of the vibrational-rotational motions on the Rydberg electron states in a molecule. The appropriate equations of the MQD method are derived in the present paper.

Another aspect of the problem consists in the generalization of the results of the MQD theory to the case of polyatomic molecules. The method expounded by Fano in Ref. 8 (and in other papers; see, for example, Ref. 12), and consisting in the use of appropriate boundary conditions to select a set of solutions for the Schrödinger equation, seems to us to be complicated and inconvenient for this purpose. An approach based on the integral formulation of the Schrödinger equation, which eliminates the problem of boundary conditions, turns out to be easier to generalize. With the aid of this approach we formulate in the present paper a general algorithm for the construction of a system of transcendental equations describing the energy spectrum of the Rydberg electron under conditions when there is a strong nonadiabatic coupling between the electron and the rotational motion of the molecule. The equations obtained are analyzed for molecules of the symmetric-top type. A classification of the Rydberg states of these molecules is proposed on the basis of the various series.

Considerable attention is given in the paper to diatomic molecules and, in particular, to the hydrogen

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molecule. Here the autoionization states of simple diatomic molecules are considered in detail. The vibrational-rotational autoionization rates in the various regions of the energy spectrum are computed in the particular case of the H_2 molecule.

2. THE GENERAL EQUATIONS OF THE MQD METHOD

It is convenient to consider the energy-eigenvalue problem for an electron in a molecule with the aid of the following system of integral equations:

$$\tau=\hat{t}(\hat{G}-\hat{G}_0)\tau, \quad \hat{t}=V+V\hat{G}_0\hat{t}. \tag{2}$$

Here V is the electron-ion core interaction potential, G is the Coulomb Green function, and G_0 is some single-electron Green function, chosen in accordance with the physical conditions of the problem. Equation (2) differs from the standard integral Schrödinger equation, obtained from (2) by setting $G_0=0$, in having the vertex part and the basis of the intermediate states renormalized. The integral equation (2) can be significantly simplified and in certain cases solved when there are data on the matrix elements of the t-operator.

Let us first consider the adiabatic problem. The Coulomb Green function of a highly excited electron can be represented in the form

$$\hat{G}(E)=\sum_{nlm}\frac{|nlm\rangle\langle nlm|}{E-E_n}+\hat{G}_0(E), \tag{3}$$

where the $|nlm\rangle$ are the wave functions of the discrete spectrum, l and m being the electron angular momentum and its component along a prescribed axis. As regards the function $G_0(E)$, which is defined in such a way as to include the states of the continuous spectrum $|klm\rangle$, it is known that it is a smooth function of the electron energy. Thus, we obtain from (2) with allowance for (3) the following system of equations:

$$\tau_{nlm}=\sum_{n'l'm'}\frac{\langle nlm|\hat{t}|n'l'm'\rangle}{E-E_{n'}}\tau_{n'l'm'}. \tag{4}$$

For any potential V that strongly distorts the Coulomb interaction between the electron and the ion core at small distances and decreases not slower than $\sim 1/r^2$ for $r\to\infty$, the range of electron coordinates that makes the dominant contribution to the matrix elements of the t-operator is significantly smaller than the radius $r\sim n^2$ of the outer electron's orbit (it is then assumed that $\lim Vr^2\to 0$ as $r\to 0$). For this reason, the matrix elements of the t-operator can be considered to be weakly dependent on the electron energy (for example, on a scale $\sim 1/n^3$), which allows us to represent them in the form

$$\langle nlm|\hat{t}|n'l'm'\rangle=\frac{C^{ll'}_{mm'}(\xi)}{n^{3/2}n'^{3/2}}. \tag{5}$$

The representation (5) is valid for any relation between the quantum numbers n and n' if $V(r)$ decreases faster than $1/r^2$, and for $|n-n'|\ll n$ if $V(r)\sim 1/r^2$.

Let us now assume that the interaction of the electron with the ion core is axially symmetric, not depending on the azimuthal angle, φ, of the internal rotation. Then the matrix of the t-operator is diagonal in m, i.e.,

$$C^{ll'}_{mm'}(\xi)=C^{ll'}_{\Lambda}(\xi)\delta_{mm'}, \quad \Lambda=|m| \tag{6}$$

(at $\Lambda>0$ the adiabatic states are twofold degenerate with respect to a change of sign of $\pm\Lambda$). Taking out in (4) from under the sign of summation over n' the factors that depend weakly on the energy, we find that for $n\gg 1$

$$\tau_{l\Lambda}=-\pi\operatorname{ctg}\pi\mu_{\Lambda}(\xi)\sum_{l'}C^{ll'}_{\Lambda}(\xi)\tau_{l'\Lambda}. \tag{7}$$

For the variables $\cot\pi\mu_{\Lambda}(\xi)$, the equations obtained are algebraic and describe series of Rydberg levels under adiabatic electron-motion conditions. It is important for what follows that we be able to relate the coefficients $C^{ll'}_{\Lambda}$ with the experimentally observable adiabatic shifts $\mu_{\Lambda}(\xi)$ or intensities of the corresponding spectral lines. We shall assume that these coefficients are known. Let us note in this connection that the two-channel QD theory developed by Fano for diatomic homonuclear molecules[8] operates with two adiabatic parameters, C_{σ} and C_{π}, corresponding to the σ and π states of the Rydberg electron ($l=l'=1$).

To investigate the problem with allowance for the internal degrees of freedom of the molecule, we turn to Eq. (2) with the Green-function operator defined as

$$\hat{G}(E)=\sum_{nlqJM}\frac{|nlqJM\rangle\langle nlqJM|}{E+1/2n^2-E_q}+\hat{G}_0, \tag{8}$$

where q is the set of vibrational and rotational quantum numbers and E_q is the energy associated with the internal motion of the nuclei. Let us choose the function G_0 in the form

$$\hat{G}_0(E)=\sum_{klqJM}\frac{|klqJM\rangle\langle klqJM|}{E-k^2/2}, \tag{9}$$

then the t-operator is defined in the same way as in the adiabatic case. For definiteness, we restrict ourselves to the case of the singlet states of the molecule, when the angular momentum J, the resultant of the orbital angular momentum of the electrons and the angular momentum of the nuclei, and its component M along a given axis are integrals of the motion.

Further discussion requires more detailed information about the structure of the rotational spectrum of the molecules. It seems most natural to begin it with the case of molecules of the symmetrical-top type. This case, on the one hand, includes linear molecules and molecules of the spherical-top type and, on the other, forms a basis for a further generalization of the theory to the case of an arbitrary type of molecule.

3. THE RYDBERG STATES IN MOLECULES OF THE SYMMETRICAL TOP TYPE

To molecules of the symmetrical-top type pertain polyatomic molecules possessing a natural symmetry about the internal-rotation axis. To them may also be roughly referred molecules two of whose principal moments of inertia are for some reason nearly equal to each other.

In order not to complicate the problem from the very beginning, let us exclude the vibrational degrees of freedom from consideration. Let us write the rotational ion-core Hamiltonian for the symmetrical top in the form

$$\hat{H}_{\text{вр}}(\mathbf{R},\xi)=B\hat{N}^2+(A-B)\hat{K}^2. \tag{10}$$

Here A and B are the corresponding rotational constants, R is the coordinate of the center of gravity of the system, $\hat{N}$ is the core's angular momentum operator, and $\hat{K}$ is the operator corresponding to the component N of the angular momentum along the symmetry axis.

The eigenfunctions of the Hamiltonian (10) have the form^{22}

$$\varphi^N_{N_z K}=[(2N+1)/8\pi^2]^{1/2}D^N_{N_z K}(\chi,\theta,\phi), \tag{11}$$

where N_z is the component of the angular momentum N along the fixed axis, z, and χ, θ, and ϕ are the corresponding Euler angles specifying the position of the molecule.

We can, in accordance with the addition rules for angular momenta, write the normalized total angular function of the compound (electron + ion core) system possessing a total angular momentum J and a component M along the z axis in the form

$$\Phi^{JM}_{lNK}(\hat{r}\hat{R},\xi)=\sum_m Y_{lm}(\vartheta,\varphi)D^N_{M-mK}(\chi,\theta,\phi)[(2N+1)/8\pi^2]^{1/2}(lN,mM-m|JM). \tag{12}$$

Here $Y_{lm}(\vartheta,\varphi)$ is the spherical harmonic of an electron with the angles ϑ and φ in the fixed system of coordinates, $D^N_{M-mK}(\Omega)$ is a generalized spherical harmonic, and the $(lN,mM-m|JM)$ are the coefficients arising from the vector addition.

Substituting the angle function (12) into the formulas (8) and (9), we obtain in place of the integral equation (2) the expression

$$\tau_{nlNKJM}=\sum\tau_{n'l'N'K'J'M'}\frac{\langle nl|S^{lNK,l'N'K'}_{JM,J'M'}(r,\xi)|n'l'\rangle}{E+1/2n'^2-BN'(N'+1)-(A-B)K'^2}, \tag{13}$$

where the summation is performed over the primed indices, the $|nl\rangle$ are the radial Coulomb wave functions, and

$$S^{lNK,l'N'K'}_{JM,J'M'}(r,\xi)=\langle\Phi^{JM}_{lNK}|\hat{t}(\mathbf{r}-\mathbf{R},\xi)|\Phi^{J'M'}_{l'N'K'}\rangle. \tag{14}$$

The computation with the formula (14) of the diagonal —in m—adiabatic reaction matrix (6) leads to the following expression:

$$S^{lNK,l'N'K'}_{JM,J'M'}=\sum_{s,j}(-1)^{s+l+l'+N+J}[(2j+1)(2N+1)]^{1/2}\delta_{JJ'},\delta_{MM'},\delta_{KK'}$$

$$\cdot C^{ll'}_{|s|}(r,\xi)(l'l,s-s|j0)(jN,0-K|N'-K)W(ll'NN';jJ), \tag{15}$$

$$C^{ll'}_{|s|}(r,\xi)=\langle Y_{ls}|\hat{t}|Y_{l's}\rangle, \tag{16}$$

$W(ll'NN';jJ)$ are the Racah coefficients. It can be seen from (15) that the electron–rotating core interaction potential V is diagonal in the total angular momentum J, in its component M along the axis of quantization, and in the component K of the angular momentum of the nuclei along the axis of symmetry of the molecule, and mixes the states with different values of the angular momentum N of the nuclei and of the component Λ of the electron's orbital angular momentum.$^{1)}$ Let us recall that the mixing of the states with different l occurs even in the adiabatic limit [see the formula (5)], and is due to the fact that the interaction potential V is, in the general case, not invariant under the replacement of the electron's polar angle ϑ by $\pi-\vartheta$.

It also follows from the expressions (14) and (15) that the matrix of the t-operator is invariant under simultaneous transposition of the indices l and N, i.e.,

$$S^{lNK,l'N'K'}_{JM,J'M'}=S^{l'N'K,lNK'}_{JM,J'M'}. \tag{17}$$

Since the dominant contribution to the matrix elements (5) is made by the region of small r, where the Coulomb radial wave functions behave like^{20} $\sim r^l$, let us restrict ourselves to consideration of the coupling of the S and P states. Evidently, only the σ ($\Lambda=|m|=0$) states can be mixed, whereas the π and σ states do not interact with each other. Then the system of equations determining the set of Rydberg states of the molecules for arbitrary J and K assumes the following form:

$$\tau_{lNK}=\sum_{l'N'}A^{ll'}_{JKNN'}\operatorname{ctg}\pi\nu_{N'K}\tau_{l'N'K}. \tag{18}$$

Here $\nu_{NK}(E)$ is the effective principal quantum number of a Rydberg state belonging to a given series, i.e.,

$$\nu_{NK}(E)=n-\mu_{NK}(E)=\{2[BN(N+1)+(A-B)K^2-E]\}^{-1/2}. \tag{19}$$

For fixed values of the quantum numbers J and K there are in the general case three pairs of series, corresponding respectively to the various N values,$^{2)}$

$J-1,\quad J,\quad J+1.$

In this case each of these series pairs converges to its ionization limit. The coefficients, $A^{ll'}_{JKNN'}$, in the system of equations (18) are defined as

$$A^{ll'}_{JKNN'}(\xi)=\pi\begin{cases}C_\sigma^{00}(\xi)\delta_{NN'}, & l=l'=0,\\ \sum_\Lambda \alpha^{(\Lambda)}_{JKNN'}C_\Lambda^{11}(\xi), & l=l'=1,\\ C_\sigma^{01}(\xi)(-1)^{N+N'}(N1,-K0|N'-K)\delta_{JN}, & \\ l=0,\quad l'=1, & \end{cases} \tag{20}$$

where the $C^{ll'}_\Lambda(\xi)$ are the corresponding adiabatic coefficients [see (6)] and the $\alpha^{(\Lambda)}_{JKNN'}$ for $\Lambda=0$ and 1 are equal to

$$\alpha^{(\Lambda)}_{JKNN'}=\frac{(1+\Lambda)}{3}\delta_{NN'}+(-1)^{\Lambda+N+J}\gamma_{JKNN'}, \tag{21}$$

$$\gamma_{JKNN'}=[10(2N+1)/3]^{1/2}(2N,0-K|N'-K)W(11NN';2J).$$

The expression (20) for $l=1$ and $l'=0$ are, according to (17), obtained by simultaneously transposing the lN and $l'N'$. The system of equations (18), together with the formulas (19)–(21), can be applied to all kinds of molecules of the symmetrical-top type (including the spherical top, i.e., the case in which $A=B$); the transition to diatomic (or arbitrary linear) molecules here is obvious: it is sufficient to set $K=0$ in (19)–(21).

Let us now proceed to analyze the system of equations (18) and classify the electron-rotational Rydberg states for the important case of the $J=1$ states, which can be populated in the process of photoabsorption by the unexcited molecules. The rotational states of the symmetrical top in the ground, nondegenerate vibrational state can be classified according to the values of the quantum number K. For definiteness, let us analyze the spectra of molecules whose symmetry is specified by the group C_{3v} (i.e., molecules of the type XY_3). Then states of symmetry E are realized for a K value that is not a multiple of three states of the A symmetry for a K value that is a multiple of three (these states do not interact with each other, i.e., $A \nleftrightarrow E$). In the case under consideration N assumes the values 0, 1, 2 for $K=0$, ± 1, ± 2, respectively; therefore, to the E-type (twofold degenerate) states correspond the values $N=1$, 2, and $K=\pm 1$, ± 2, while to the A-type states correspond $N=0, 1, 2$ and $K=0$ (non-degenerate states).

Let us first analyze the states of the type E. For the $|K|=1$ case, equating the determinant of the system (18) to zero, we find

$$(a-\operatorname{tg}\pi\nu_{11})(b-\operatorname{tg}\pi\nu_{11})(b-\operatorname{tg}\pi\nu_{21})=-2fd^2 +d^2(b-\operatorname{tg}\pi\nu_{11})+d^2(b-\operatorname{tg}\pi\nu_{21})+f^2(a-\operatorname{tg}\pi\nu_{11}); \tag{22}$$

$$a=\pi C_\sigma^{00}, \quad b=\pi(C_\sigma^{11}+C_\pi^{11})/2, \quad f=\pi(C_\sigma^{11}-C_\pi^{11})/2, \quad d=-\pi\dot{C}_\sigma^{01}/\sqrt{2}. \tag{23}$$

It can be seen from (22) that the energy spectrum of the molecule contains three Rydberg-level series, two of which have the same ionization limit, and correlate at small n with the split σ doublet, while the third series correlates with the π state. The distance between the corresponding ionization limits is equal to $4B$. Thus, the Rydberg series can be classified according to the total angular momentum J, the ionization limit (determined by the quantum numbers N and K), and the type of adiabatic molecular orbital with which the states with small n correlate.

If the interaction potential $V(\mathbf{r}-\mathbf{R}, \xi)$ is invariant under reflection in a plane perpendicular to the axis of symmetry of the molecule, then all the matrix elements that are off-diagonal with respect to l vanish. Then $d=0$, and Eq. (22) describes the independent states with $l=0$ and the two groups of interacting levels with $l=1$.

For the $|K|=2$, $N=N'=2$ case, we obtain a single twofold degenerate—with respect to $\pm K$—series of π states with energy

$$E_n=2B+A-1/2(n-\mu_\pi)^2. \tag{24}$$

Let us now investigate the important case $K=0$ (i.e., the case of the nondegenerate, A-type states). Here $N, N'=0, 1, 2$. The condition for the system of equations (18) to have a unique solution in this case yields the relations

$$\nu_{10}=n-\mu_\pi \tag{25}$$

and

$$(a-\operatorname{tg}\pi\nu_{00})(b-\operatorname{tg}\pi\nu_{10})(d-\operatorname{tg}\pi\nu_{20})=fg^2 +g^2(a-\operatorname{tg}\pi\nu_{00})+f^2(b-\operatorname{tg}\pi\nu_{10})/2+g^2(d-\operatorname{tg}\pi\nu_{20})/2, \tag{26}$$

where the coefficients are equal to

$$a=\pi(C_\sigma^{11}+2C_\pi^{11})/3, \quad b=\pi C_\sigma^{00}, \quad d=\pi(2C_\sigma^{11}+C_\pi^{11})/3, \quad f=-2\pi(C_\sigma^{11}-C_\pi^{11})/3, \quad g=-\pi\sqrt{2}C_\sigma^{10}/\sqrt{3}. \tag{27}$$

Consequently, there are three Rydberg-level series, which correspond to different ionization limits, and correlate, as $Bn^3 \to 0$, respectively to the P_σ, S, and P_π states (the para modification), and a separate ν_{10} series of π states (the ortho modification).

The case in which the interaction potential V is invariant under reflection in a plane perpendicular to the axis of symmetry of the molecule corresponds to the case of homonuclear diatomic molecules X_2.

To consider the most interesting situation, which is the situation with $l=1$, we set $K=0$ in the general formulas (19)–(21), and retain only those matrix elements for which $l=l'=1$. Since the coefficients

$$(2N,\, 00|N'0)=(-1)^{N-N'}(2N,\, 00|N'0)$$

in expression (21) are different from zero only when

$$N-N'=2s \quad (s=0, \pm 1, \pm 2, \ldots),$$

only the two possibilities

$$N,\ N'=0,\ 2 \text{ and } N=N'=1$$

are realized in the system. For the first of them we have the equation[3)]

$$(A_{00}-\operatorname{tg}\pi\nu_0)(A_{22}-\operatorname{tg}\pi\nu_2)=A_{02}^2; \quad A_{00}=-(\operatorname{tg}\pi\mu_\sigma+2\operatorname{tg}\pi\mu_\pi)/3, \tag{28}$$

$$A_{22}=-(2\operatorname{tg}\pi\mu_\sigma+\operatorname{tg}\pi\mu_\pi)/3, \quad A_{02}=\sqrt{2}(\operatorname{tg}\pi\mu_\sigma-\operatorname{tg}\pi\mu_\pi)/3 \tag{29}$$

(μ_σ and μ_π are the adiabatic quantum shifts of the σ and π states[1,2]), while the second series is found to consist of the terms corresponding to the $nP_\pi\Pi_u$ ortho-modification of the X_2 molecule ($N=1$), which do not interact with the rotational motion of the molecule [the generally accepted designation of this series is[1,2] $Q(1)$].

4. THE AUTOIONIZATION RYDBERG STATES OF A DIATOMIC MOLECULE X_2

Let us now consider both the rotational and the vibrational degrees of freedom of the molecules. Of great importance for the determination of the nonadiabatic coupling between the electronic and vibrational motions is the smallness of the parameter, η, characterizing the ratio of the vibration amplitude to the interatomic distance. It is precisely this circumstance that allowed us to investigate the electronic-rotational spectra without allowance for the vibrations of the molecules. The vibrational transitions are, however, quite important in those cases in which they lead to the interaction of the states with a continuous spectrum, as a result of which interaction the discrete levels acquire autoionization widths. Here we focus our main attention on the investigation of the autoionization states with allowance for the nonadiabatic coupling of the electron motion with the vibrational-rotational motion.

The equation determining the energy levels in the case n question has the form[4)]

$$\operatorname{Det}|A_{NN'}^{vv'}-\operatorname{tg}\pi\nu_{N'v'}\delta_{NN'}\delta_{vv'}|=0, \tag{30}$$

where the $A_{NN'}^{vv'}$ are the corresponding matrix elements:

$$A_{NN'}^{vv'}=\langle v|A_{NN'}(R)|v'\rangle, \tag{31}$$

the $|v\rangle$ are the wave functions for the vibrational motion in the ground electronic state of X_2^+, the $A_{NN'}(R)$ are given by the expressions (29),

$$\nu_{Nv}=n-\mu_{Nv}=\{2[E_v+BN(N+1)-E]\}^{-1/2}, \tag{32}$$

and E_v is the energy associated with the vibrational motion of the nuclei.

Since the quantum defect depends weakly on R, we can, in considering the combined effect of the vibrational and rotational motions on the electron energy levels, restrict ourselves to the one-quantum transition (i.e., $\Delta v=\pm 1$) approximation. Setting, for definiteness, v, $v'=0, 1$ in Eq. (30), and introducing the following notation:

$$\begin{gathered} x_0=A_{00}{}^{00}, \quad y_0=A_{00}{}^{10}, \quad z_0=A_{00}{}^{11}, \\ x_1=A_{20}{}^{00}, \quad y_1=A_{20}{}^{10}, \quad z_1=A_{20}{}^{11}, \\ x_2=A_{22}{}^{00}, \quad y_2=A_{22}{}^{10}, \quad z_2=A_{22}{}^{11}, \end{gathered} \tag{33}$$

we obtain a 4×4 determinant, from which it is convenient for the investigation of the decay characteristics of the Rydberg states to separate the diagonal blocks

$$\begin{aligned} D_0(E)&=(x_0-\operatorname{tg}\pi\nu_{00})(x_2-\operatorname{tg}\pi\nu_{20})-x_1{}^2, \\ D_1(E)&=(z_0-\operatorname{tg}\pi\nu_{01})(z_2-\operatorname{tg}\pi\nu_{21})-z_1{}^2, \end{aligned} \tag{34}$$

which determine in the zeroth approximation Rydberg-electron-energy-level series with different ion-core vibrational energies (in the present case these are $v=0$ and $v=1$). Then Eq. (30) assumes the form

$$D_0(E)D_1(E)=F_{01}(E), \tag{35}$$

where the off-diagonal—with respect to v—right-hand side characterizes the nonadiabatic coupling of the electron-rotational states to the vibrational motion of the molecule's nuclei, and is defined as

$$\begin{gathered} F_{01}=2x_1z_1(y_0y_2+y_1{}^2)+(x_0-\operatorname{tg}\pi\nu_{00})[y_2{}^2(z_0-\operatorname{tg}\pi\nu_{01}) \\ +y_1{}^2(z_2-\operatorname{tg}\pi\nu_{21})-2y_1y_2z_1]+(x_2-\operatorname{tg}\pi\nu_{20})[y_0{}^2(z_2-\operatorname{tg}\pi\nu_{21}) \\ +y_1{}^2(z_0-\operatorname{tg}\pi\nu_{01})-2y_0y_1z_1]-2x_1y_1[y_0(z_2-\operatorname{tg}\pi\nu_{21}) \\ +y_2(z_0-\operatorname{tg}\pi\nu_{01})]+2y_0y_1{}^2y_2-y_0{}^2y_2{}^2-y_1{}^4. \end{gathered} \tag{36}$$

First of all, let us find the rotational autoionization rate in the Beutler region of the spectrum,

$$0<E_\lambda<6B \tag{37}$$

[where E_λ is the corresponding root of the equation $D_0(E)=0$], in the zeroth approximation with respect to $F_{01}(E)\sim y^2\ll 1$. With this aim in view, let us set $\nu_{00}=i\gamma_{00}$, $\nu_{20}\approx\nu_{20}^{(0)}-i\varkappa_{20}^{(0)}$, where $\gamma_{00}\gg 1$. Separating in the equation

$$D_0(i\gamma_{00},\nu_{20})=(x_0-i)[x_2-\operatorname{tg}\pi(\nu_{20}^{(0)}-i\varkappa_{20}^{(0)})]-x_1{}^2=0$$

the real and imaginary parts, and solving the corresponding system of equations, we finally obtain

$$\varkappa_{20}^{(0)}=\pi^{-1}\operatorname{arcth}\left(\frac{1}{2b}\{a^2+b^2+1-[a^2(a^2+2b^2+2)+(b^2-1)^2]^{1/2}\}\right), \tag{38}$$

where

$$a=x_2-x_0x_1{}^2/(1+x_0{}^2), \qquad b=x_1{}^2/(1+x_0{}^2).$$

The autoionization rate is given by the expression

$$\Gamma_{20}^{(0)}=2\varkappa_{20}^{(0)}/\nu_{20}{}^3. \tag{39}$$

It follows from (38) that in the limit of small adiabatic quantum shifts, i.e., for $\pi\mu_\Lambda\ll 1$, $\varkappa_{20}^{(0)}\approx x_1{}^2/\pi$, and the autoionization rate is equal to

$$\Gamma_{20}^{(0)}\approx\frac{4\pi}{9}\frac{(\mu_\sigma-\mu_\pi)^2}{\nu_{20}{}^3}, \tag{40}$$

i.e., we obtain the result presented in Ref. 1.

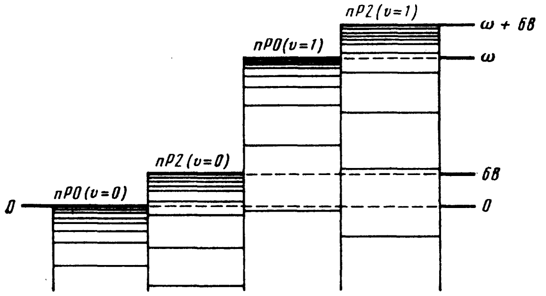

FIG. 1. Schematic arrangement of the Rydberg levels of a diatomic molecule X_2.

We limit ourselves to the consideration of the autoionization states belonging to the region $0<E_\lambda<\omega+6B$ (ω is the vibration frequency of the ion core). The following situations are possible here (see Fig. 1):

a) one channel is closed and three are open, i.e., $\omega<E_\lambda<\omega+6B$;

b) two channels are closed and two are open, i.e., $6B<E_\lambda<\omega$;

c) three channels are closed and one is open, i.e., $0<E_\lambda<6B$.

Let us first analyze the case a). In this case the E_λ are a set of roots of the equation, $D_1(E)=0$, corresponding to the $nP2(v=1)$ level series. Setting in (35) $\nu_{N0}=i\gamma_{N0}$, $\nu_{01}=i\gamma_{01}$, and $\nu_{21}\approx\nu_{21}^{(0)}+\delta E_\lambda\nu_{21}^{(0)3}$, and taking into account the fact that $\delta E_\lambda\nu_{21}^{(0)3}\ll 1$, while $\gamma_{Nv}\gg 1$, we have

$$\delta E_\lambda=-\frac{F_{01}(E_\lambda)\cos^2\pi\nu_{21}^{(0)}}{\pi\nu_{21}^{(0)3}D_0(i\gamma_{00},i\gamma_{20})(z_0-i)}.$$

Using the relation

$$\cos^{-2}\pi\nu_{21}^{(0)}=1+[z_2-z_1{}^2/(z_0-i)]^2,$$

we finally obtain

$$\begin{gathered} \Gamma(E_\lambda)=\frac{2}{\pi\nu_{21}{}^3}(\pi\varkappa_{21}^{(0)}+\Delta(E_\lambda)), \\ \Delta(E_\lambda)=\operatorname{Im}\left\{\frac{F_{01}(E_\lambda)(z_0-i)}{D_0(i\gamma_{00},i\gamma_{20})[(z_0-i)^2+(z_2(z_0-i)-z_1{}^2)^2]}\right\}, \end{gathered} \tag{41}$$

where $\varkappa_{21}^{(0)}$ is given by the formula (38) with the matrix elements x_i replaced by the z_i. The first term in (41) describes the rotational autoionization, while the second gives the additional contribution to the autoionization rate due to the nonadiabatic coupling to the states of the vibrationally unexcited molecules [i.e., the $nPN(v=0)$ states]. Notice that the formula (41) gives the total autoionization-level width.

Next, let us investigate the case b), in which E_λ denotes the set of roots of the equation $D_1(E)=0$ pertaining to the $nPN(v=1)$ series. Setting $\nu_{N0}=i\gamma_{N0}(\gamma_{N0}\gg 1)$ and $\nu_{N1}\approx\nu_{N1}^{(0)}+\delta E_\lambda\nu_{N1}^{(0)3}$, and also taking into account the fact that $\delta E_\lambda\nu_{N1}^{(0)3}\ll 1$, we obtain

$$\Gamma(E_\lambda)=\frac{2}{\pi}\left\{\sum_N\frac{(z_N-\operatorname{tg}\pi\nu_{N1})}{\cos^2\pi\nu_{N1}}\nu_{N1}{}^3\right\}^{-1}\operatorname{Im}\left[\frac{F_{01}(E_\lambda)}{D_0(i\gamma_{00},i\gamma_{20})}\right]. \tag{42}$$

Let us now consider the case c). If E_λ belongs to the $nP2(v=0)$ series, then the autoionization width is determined by the formulas (38) and (39), i.e., the detachment of the electron is realized through a rotational transition. For the $nPN(v=1)$ series, however, the autoionization rate is given by the formula (42) with $i\gamma_{20}$ replaced by $\nu_{20}(E_\lambda)$.

5. THE AUTOIONIZATION OF MOLECULAR HYDROGEN

Let us use the formulas obtained to compute the autoionization rate for the Rydberg states of the H_2 molecule. The consideration of this case is of special interest both in view of the practical importance of the hydrogen molecule in a variety of physical processes and as a result of the fact that these molecules are the simplest, best studied molecular object on which the various theoretical approaches can be tested. We shall be guided by the case of the para-states of H_2 [i.e., the case of the $R(0)$-type series[1,2]], in which the nonadiabatic effects couple the greatest number of channels, and which are the most complicated for a theoretical investigation.

Using the data given in Ref. 1 for $\mu_\Lambda(R)$, we find from the formulas (29), (31), and (33) the following numerical values for the parameters x_i, y_i, and z_i:

$$\begin{aligned} &x_0=-0.07, \quad y_0=-0.04, \quad z_0=-0{,}10,\\ &x_1=0.45, \quad y_1=0.10, \quad z_1=0{,}50,\\ &x_2=-0.39, \quad y_2=-0.11, \quad z_2=-0.45. \end{aligned} \qquad (43)$$

In the case a) of three open channels, a computation with the formula (41) and the parameter values given in (43) yields $\varkappa_{21}^{(0)}=0.067$ and $\Delta(E_\lambda)=0.008$ [here $\Delta(E_\lambda)$ is practically independent of the level energy]. For example, for the $26P2(v=1)R(0)$ level we find $\Gamma=1.9$ cm^{-1}. The theoretical value computed in Ref. 1 from the formula (40) is equal to $\Gamma=1.7$ cm^{-1}, while experiment[1] gives the value $\Gamma=2.3$ cm^{-1}. Thus, the possibility of autoionization with a change in the vibrational state of the core leads to an increase in the decay rate.

In Table I we present the autoionization widths of the low-lying Rydberg levels of H_2 in the region $6B<E<\omega$, as computed from the formula (42) with the initial data (43). The results are compared with those of other authors' approximate computations, performed either in the two-channel approximation without allowance for the electron-rotational motion coupling,[9-11] or with allowance for this coupling, but without allowance for the combined effect of the vibrational-rotational transitions and under the implicit assumption that the adiabatic Rydberg level shifts are small.[2] Our results differ from the results obtained in Refs. 2, 9–11. Moreover, as follows from Table I, there is at present no clear-cut quantitative agreement among the experimental data of the various authors. This circumstance, as well as the paucity of experimental data, indicates definite difficulties in measuring the autoionization rates. Therefore, the theoretical computation clearly assumes primary significance here.

TABLE I. Autoionization widths (in cm^{-1}) of the low-lying Rydberg levels of the H_2 molecule ($v=1$) for the optical $R(0)$ series (the state of theory and experiment).

Level nPN $(v=1)$	Theoretical data*					Experimental data			
	a	*b*	*c*	*d*	*e*	Ref. 1	Ref. 2	Ref. 3	Ref. 4
8*P*0	2,1	3.7	1.1	3,7	2.14	5.8	5.1	2.1	4.0
8*P*2	1.9	1.0	1.1	2.7	1.48	–	2.8	–	3.0
9*P*0	1.5	4.9	–	1.7	1.17	–	2.4	–	–
9*P*2	1.4	7.6	8.0	2.9	1.89	–	2.3	–	–
10*P*0	–	2.3	–	0.6	0,43	–	0.9	–	–
10*P*2	–	6.5	–	2.7	1.33	–	–	–	–
11*P*0	–	–	–	0.1	0.09	–	1.3	–	–

*a)–c) Results respectively obtained in Refs. 9–11 in the simplest two-channel approximation; d) Dehmer and Chupka's computed data[2]; e) our results.

TABLE II. Autoionization widths of high-lying Rydberg levels of the H_2 molecule for the optical $R(0)$ series ($v=1$).

Level nPN	Γ, cm^{-1}		Level nPN	Γ, cm^{-1}		Level nPN	Γ, cm^{-1}	
	a *	*b* **		*a*	*b*		*a*	*b*
12*P*0	1,08	1,7	21*P*0	0.04	0.0	32*P*0	0.00	0.0
11*P*2	0,11	0.2	22*P*0	0.17	0.2	33*P*0	0.01	0,0
13*P*0	0.49	0,8	17*P*2	0,16	0,3	34*P*0	0.03	0.0
12*P*2	0.60	1,0	23*P*0	0,01	0.0	35*P*0	0,06	0.1
14*P*0	0.15	0,2	24*P*0	0.08	0.1	36*P*0	0.01	0.0
13*P*2	0.62	1.3	18*P*2	0,17	0,5	37*P*0	0.00	0.0
15*P*0	0,02	0,0	25*P*0	0.01	0.0	38*P*0	0.01	0.0
16*P*0	0,26	0.4	26*P*0	0,02	0.0	39*P*0	0.02	0.0
14*P*2	0,51	0.8	27*P*0	0.08	0.1	40*P*0	0.03	0.0
17*P*0	0.04	0.0	19*P*2	0.12	0,4	41*P*0	0.05	0.0
18*P*0	0.31	0.5	28*P*0	0.01	0.0	22*P*2	0.06	0.2
15*P*2	0.17	0,4	29*P*0	0.01	0.0	42*P*0	0,01	0.0
19*P*0	0.06	0.1	30*P*0	0.04	0.1	43*P*0	0.00	0.0
20*P*0	0.26	0.3	31*P*0	0.10	0.1	44*P*0	0.00	0.0
16*P*2	0.11	0.2	20*P*2	0,07	0.2	45*P*0	0.01	0.0

*a) Results of calculation with the formula (42) and effective quantum numbers ν_{01} and ν_{21} taken from Ref. 2.
**b) Results of Dehmer and Chupka's calculation.[2]

In Table II we present the autoionization widths of all the experimentally observed high-lying levels, as computed from the formula (42) with the initial data (43). For the majority of levels, this is the first time that the $\Gamma(E)$ values have been given. Allowance for the finite level shift in the formula (41) is equivalent to allowance for the interaction of the level in question with the surrounding levels. Such an interaction stabilizes the states against any external influence, in general, and decay, in particular. For this reason, the autoionization-width calculations performed within the framework of the simplified model of Ref. 2 yield overestimated results. The $\Gamma(E)$ values given in Tables I and II can be used directly in calculations connected with resonance photoionization, i.e., the process underlying the new physical method of detecting vibrationally excited H_2 molecules.

In conclusion, let us note that the method, developed in the present paper, of investigating the Rydberg states of molecules admits of further generalizations. Of great interest are, in particular, polyatomic molecules, in considering which we can neglect the rotational motion, but should take into account the multimode character of the vibrational motion. Also of specific interest are the predissociation Rydberg states of molecules in which the nuclear motion is characterized by a continuous spectrum. It should, however, be borne in mind that the proposed approach requires the knowledge of the adiabatic reaction matrix (5), which makes the development of the MQD method dependent on the experimental spectroscopic investigation of the first terms of the Rydberg series.

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1)Let us note that, generally speaking, the potential V also depends on the azimuthal angle φ of the internal rotation in a way that duplicates the axial symmetry of the molecule. Therefore, in principle, the scattering of the electron by the core is accompanied by a change in K, which can be incorporated without any difficulty into the above-expounded computational scheme. However, the deviations of V from the φ-averaged value $\bar{V}$ are, as a rule, small, and can, in the first approximation, be neglected.

[2] For $J=0$, there will be two such pairs of series, corresponding to $N'=0$ and $N'=1$.

[3] We can, by setting $\nu_0 = n - \mu_0$, easily verify directly that Eq. (28) coincides with Eq. (32) of Ref. 8.

[4] For the case in which the a diabatic Rydberg shifts are small (i.e., $\pi\mu_\Lambda \ll 1$), Eq. (30) goes over into Eqs. (25) and (28) of Ref. 12, which are derived through a direct expansion of the two-channel equations describing the nonadiabatic coupling of the electron motion to the molecule's rotational motion in terms of the vibrational states of He$^+$. This procedure cannot, however, be considered to be consistent enough, since the result depends on the way the basic two-channel equations are written. Our method, on the other hand, precludes any ambiguity in the solution of the problem, and leads to equations that, for $\pi\mu_\Lambda \sim 1$, differ from those formulated in Ref. 12.

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