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Complex quantum defects of superexcited Rydberg states of H_2

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The $\underline{R}$-matrix method for electron-molecule collisions has been applied to autoionizing doubly excited adiabatic states of H_2 with ${}^1\Sigma_g^+$ symmetry for internuclear distances from 1 to 5 a.u. Above the previously known three states we have found many other doubly excited states for the first time. These states are classified into two Rydberg series, namely, $(1\sigma_u)(np\sigma)$ and $(1\sigma_u)(nf\sigma)$ series up to $n=10$. They are characterized by their complex quantum defect, the imaginary part corresponding to the width of each Rydberg state. For the smaller internuclear distances R these Rydberg states are isolated resonances, but for $R>4$ a.u. some of them begin to overlap and present a problem of multichannel autoionizing Rydberg series, although there is only one common series limit in the present case. This work exemplifies the usefulness of the $\underline{R}$-matrix method for studying molecular doubly excited Rydberg states.

I. INTRODUCTION

Highly excited Rydberg states of atoms have been studied extensively in recent years because of their unique physical properties; they are quite stable against radiative decay, but are highly reactive to charged particles and to external fields due to their weak binding and to the large size of the electron cloud.[1] The binding energy $E(\infty)-E(n)$ of a single-channel Rydberg electron in a neutral atom may be represented by the Rydberg formula $E(\infty)-E(n)=[n-\mu(n)]^{-2}$ Ry with a quantum defect $\mu(n)$ which is usually a slowly varying function of the principal quantum number n. This quantum defect arises from occasional elastic collisions between the Rydberg electron and the residual ion core. If an electron in the ion core is excited then the collisions may be superelastic, in which case the Rydberg electron may acquire enough energy to escape from the ion core. In other words a two-electron excited Rydberg atom, or doubly excited Rydberg atom, has a finite lifetime in the absence of a radiation field. Therefore, its energy eigenvalue $E(n)$ is complex, the imaginary part $-\frac{1}{2}\Gamma(n)$ being the half-width of this decaying state. One may modify the Rydberg formula by replacing the quantum defect $\mu(n)$ by a complex quantity $q(n)=\mu(n)+i\gamma(n)$ for the purpose of representing the complex energies,[2,3] namely,

$$E(\infty)-E(n)=\{n-[\mu(n)+i\gamma(n)]\}^{-2}$$
$$\simeq[n-\mu(n)]^{-2}+2i\gamma(n)[n-\mu(n)]^{-3} \quad (1)$$

in rydbergs, where the last approximate expression is valid for $\gamma^2 \ll (n-\mu)^2$. One may refer to $q(n)$ as a complex quantum defect. The first term on the right-hand side of Eq. (1) is the usual Rydberg formula. The second term representing the width is appropriate for high Rydberg states as is seen from the normalization constant of the Rydberg wave function.

Doubly excited Rydberg states of molecules are superexcited states, and have many different decay channels, namely, (1) dissociation channels in which neutral fragments or a fragment ion pair may be produced in the ground or excited states, and (2) electron-ion scattering channels in which the nuclear as well as the electronic motion of the molecular ion may be excited. If the ion is formed in a repulsive state, it may dissociate into ionic and neutral fragments. Doubly excited molecular Rydberg states M^{**} may be formed from any of these channels, by single-photon or multiphoton absorption, or by electron-impact excitation. Therefore these states may play an important role as intermediate resonance states in (for example, for the hydrogen molecule) elastic scattering[4-7]

$$e+H_2^+ \rightarrow H_2^{**} \rightarrow H_2^+ + e\ ,$$

vibrational excitation[8]

$$e+H_2^+(v) \rightarrow H_2^{**} \rightarrow H_2^+(v')+e\ ,$$

dissociative recombination[8-10]

$$e+H_2^+ \rightarrow H_2^{**} \rightarrow H+H^*\ ,$$

ion-pair formation[11]

$$e+H_2^+ \rightarrow H_2^{**} \rightarrow H^+ + H^-\ ,$$

associative ionization[12,13]

$$H^+ + H^- \to H_2^{**} \to H_2^+ + e \ ,$$

$$H^* + H^* \to H_2^{**} \to H_2^+ + e \ ,$$

transfer ionization[14]

$$H^+ + H^- \to H_2^{**} \to H + H^+ + e \ ,$$

photodissociation[15]

$$h\nu + H_2 \to H_2^{**} \to H^* + H^* \ ,$$

photoionization[16,17]

$$h\nu + H_2 \to H_2^{**} \to H_2^+ + e \ ,$$

dissociative photoionization[18]

$$h\nu + H_2 \to H_2^{**} \to H_2^+ + e \to H + H^+ + e \ ,$$

resonantly enhanced multiphoton ionization and dissociation with coupling with doubly excited states[19–22]

$$h\nu + H_2^* \to H_2^{**} \to H_2^+ + e \ ,$$

$$h\nu + H_2^* \to H_2^{**} \to H + H^* \ ,$$

dissociative excitation by electron impact[23–26]

$$e + H_2 \to H_2^{**} + e \to H^* + H^* + e \ ,$$

dissociative ionization by electron impact[23,27–29]

$$e + H_2 \to H_2^{**} + e \to H + H^+ + 2e \ ,$$

and so on.

The knowledge of doubly excited *adiabatic* Rydberg states by itself is insufficient for understanding these dynamic processes. The coupling between the electronic motion and the nuclear motion is essential in general in these processes. The effect of this coupling is different depending on the process, and has to be studied separately for each process. The associated adiabatic Rydberg states are, however, common to all the processes and serve as the basis for studying them, possibly leading to a unified physical view of them. Furthermore, in some processes in which Franck-Condon transitions appear to be important, experimental measurements directly afford information on doubly excited adiabatic potential curves.[15] Thus detailed *ab initio* calculations of adiabatic Rydberg states are highly desirable. This paper reports an example of such calculations taking up a prototype problem of the hydrogen molecule with ${}^1\Sigma_g^+$ symmetry.

Being the smallest and simplest molecule, the hydrogen molecule has been studied in considerable detail in the literature. However, so far only two or three lowest-lying doubly excited levels of each symmetry have been computed.[4–7,30–34] In this work we calculate many more levels, which are classified into two Rydberg series and which satisfy the complex Rydberg formula (1) with a complex quantum defect varying smoothly with n.

II. THE $\underline{R}$-MATRIX METHOD

The $\underline{R}$-matrix method for electron-molecule collisions, described in detail in earlier papers[35–37] and review articles,[38–40] is particularly appropriate for the description of molecular Rydberg states. In essence, configuration space is divided into two regions by a sphere of radius a that just envelopes the electron cloud of the core states that are considered. In the inner region the Rydberg electron lies within this electron cloud and interacts strongly with the core electrons. A multicenter, configuration-interaction expansion of the total wave function is then appropriate. In the outer region, the Rydberg electron does not overlap the core electron cloud. Hence there are no electron exchange effects between the Rydberg electron and the core electrons and the interaction is weak. The wave function can then be accurately described by a single-center multichannel expansion.

The method adopted in the present calculations of the doubly excited Rydberg states of $H_2({}^1\Sigma_g^+)$ is as follows. We include two electronic channels in the outer region, namely, that associated with the ground state $1\sigma_g \ {}^2\Sigma_g^+$ of H_2^+ and that with the first excited state $1\sigma_u \ {}^2\Sigma_u^+$. The ground state is a bonding state and the first excited state is an antibonding repulsive state; see Fig. 1. The ground state of H_2^+ is coupled with $s\sigma$, $d\sigma$, and $g\sigma$ orbitals of the Rydberg electron to form a wave function of the total H_2 system of ${}^1\Sigma_g^+$ symmetry, and the first excited state is coupled with $p\sigma$, $f\sigma$, and $h\sigma$ Rydberg orbitals. Thus the wave function in the outer region is expressed as

$$\Psi_{\text{out}} = \sum_{i,l_i} \Phi_{il_i}(x_1, \hat{\mathbf{r}}_2, \sigma_2; R) F_{il_i}(r_2) \ , \tag{2}$$

where $l_i = 0$, 2, and 4 for $i = 1\sigma_g$ and $l_i = 1$, 3, and 5 for $i = 1\sigma_u$; $x_1 = (r_1, \hat{\mathbf{r}}_1, \sigma_1)$ denotes the space-spin coordinates of the core electron; $x_2 = (r_2, \hat{\mathbf{r}}_2, \sigma_2)$ those of the Rydberg electron; R is the internuclear distance; Φ_{il_i} are obtained by coupling the wave functions of H_2^+ with the angular and spin functions of the Rydberg electron; and F_{il_i} are the partial-wave channel functions of the Rydberg electron.

The core wave functions are represented by three-term linear-combination-of-atomic-orbitals molecular orbitals (LCAO MO) with optimized exponents, similar to those determined by Cohen and Bardsley[41] and employed in previous calculations of doubly excited states.[4,5] A problem arises in our case, since we are concerned with a rather large region of R in this paper. Because of multiple minima of the energy expectation value of the $1\sigma_u$ state as a function of the exponents, one of the optimum exponents for the lowest minimum grows rapidly with R around $R \simeq 2.5$ a.u. and another minimum, for which this exponent has quite a different value, becomes lower for $R > 2.8$ a.u. In other words there is an abrupt change in one of the optimum exponents, and hence in the optimized wave function, as a function of R. To avoid this unsatisfactory discontinuity we switch from one minimum to another by smoothly and artificially changing this exponent as we increase R in a small region around $R \simeq 2.5$ a.u. By a careful examination of a few different ways of smoothly changing this exponent we have been able to obtain energy expectation values that deviate from the lowest minimum only by a negligibly

TABLE I. Energy expectation values and transition moments of the two lowest states of H_2^+ represented by three-term LCAO MO. *R*, internuclear distance; *E*, total energy including the nuclear repulsion term; ΔE, error in energy; *Q*, quadrupole moment; and *D*, transition dipole. All of these quantities are given in atomic units.

		$1\sigma_g\,{}^2\Sigma_g^+$			$1\sigma_u\,{}^2\Sigma_u^+$		$1\sigma_g\,{}^2\Sigma_g^+ \to 1\sigma_u\,{}^2\Sigma_u^+$
R	*E*	ΔE	*Q*	*E*	ΔE	*Q*	*D*
1.0	−0.451 14	6.5×10^{-4}	0.093	0.435 198	1.2×10^{-5}	2.430	−0.674
1.2	−0.528 27	7.0×10^{-4}	0.139	0.244 744	1.2×10^{-5}	2.312	−0.752
1.4	−0.569 25	7.4×10^{-4}	0.196	0.102 219	1.3×10^{-5}	2.242	−0.828
1.5	−0.581 57	7.5×10^{-4}	0.230	0.043 512	1.3×10^{-5}	2.226	−0.865
1.6	−0.590 18	7.6×10^{-4}	0.268	−0.008 604	1.4×10^{-5}	2.223	−0.902
1.8	−0.599 48	7.8×10^{-4}	0.353	−0.096 660	1.5×10^{-5}	2.251	−0.975
2.0	−0.601 85	7.9×10^{-4}	0.454	−0.167 516	1.8×10^{-5}	2.322	−1.048
2.2	−0.600 05	7.9×10^{-4}	0.573	−0.224 990	2.4×10^{-5}	2.430	−1.122
2.4	−0.595 76	8.0×10^{-4}	0.712	−0.271 878	3.2×10^{-5}	2.570	−1.197
2.5	−0.593 03	8.0×10^{-4}	0.788	−0.292 034	3.8×10^{-5}	2.652	−1.235
2.6	−0.590 03	8.0×10^{-4}	0.870	−0.310 300	4.7×10^{-5}	2.740	−1.273
2.8	−0.583 55	8.0×10^{-4}	1.052	−0.341 913	6.3×10^{-5}	2.931	−1.352
3.0	−0.576 76	8.0×10^{-4}	1.256	−0.368 037	4.8×10^{-5}	3.136	−1.433
3.25	−0.568 25	8.0×10^{-4}	1.548	−0.394 490	3.0×10^{-5}	3.424	−1.538
3.50	−0.560 06	8.0×10^{-4}	1.882	−0.415 474	2.2×10^{-5}	3.753	−1.647
3.75	−0.552 37	7.9×10^{-4}	2.260	−0.432 185	1.6×10^{-5}	4.119	−1.760
4.00	−0.545 31	7.7×10^{-4}	2.683	−0.445 536	1.5×10^{-5}	4.520	−1.876
4.25	−0.538 93		3.154	−0.456 230		4.957	−1.995
4.50	−0.533 24	7.0×10^{-4}	3.673	−0.464 815	1.4×10^{-5}	5.427	−2.117
4.75	−0.528 21		4.240	−0.471 718		5.933	−2.241
5.00	−0.523 83	5.9×10^{-4}	4.854	−0.477 276	1.5×10^{-5}	6.474	−2.368
5.25	−0.520 03		5.512	−0.481 755		7.050	−2.496
5.50	−0.516 76	4.7×10^{-4}	6.214	−0.485 366	1.7×10^{-5}	7.661	−2.625
5.75	−0.513 97		6.956	−0.488 278		8.308	−2.755
6.00	−0.511 61	3.6×10^{-4}	7.734	−0.490 625	1.9×10^{-5}	8.990	−2.885

small amount compared with the difference between the lowest minimum and the exact eigenvalue. Even with this procedure the energies we have obtained are lower than those in Ref. 41 for those values of *R* for which Ref. 41 gives results. Table I shows the energy expectation values and their errors, and also the quadrupole moments and the transition dipole moments, calculated with the LCAO-MO wave functions.

In the inner region the wave function is written as a linear combination of 74 configurations

TABLE II. Positions $E_r(n)$ and widths $\Gamma(n)$ of the three lowest resonances in ${}^1\Sigma_g^+$ scattering of electrons by $H_2^+(X\,{}^2\Sigma_g^+)$ with its internuclear distance fixed at 2.0 a.u. The energies are given in atomic units.

	$\underline{R}$-matrix method				Linear-algebraic method		
	Two state+correlation			Four state	Two state	Four state	
	Present	TNS[a]	TN[b]	TN[b]	CS[c]	CS[c]	SC[d]
$E_r(2)$	0.204 2	0.2044	0.2029	0.2027	0.2219	0.2161	
$\Gamma(2)$	0.050 9	0.053	0.051	0.055	0.051	0.057	
$E_r(3)$	0.365 5	0.3661	0.3646	0.3639			0.3657
$\Gamma(3)$	0.004 96	0.005	0.0049	0.0062			0.0059
$E_r(4)$	0.398 1		0.3976	0.3973			
$\Gamma(4)$	0.001 89		0.0019	0.0024			

[a] Tennyson *et al.* (Ref. 4).

[b] Tennyson and Noble (Ref. 5).

[c] Collins and Schneider (Ref. 7).

[d] Schneider and Collins (Ref. 7).

$$\Psi_p = \mathcal{A} \sum_{i,l_i,s} \Phi_{il_i}(x_1,\hat{\mathbf{r}}_2,\sigma_2;R) f_{il_is}(r_2) c_{p,il_is} + \sum_k \phi_k(x_1,x_2;R) c_{p,k} \ , \qquad (3)$$

in which the functions $f_{il_is}(r_2)$ are numerically defined continuum basis functions centered on the center of gravity and satisfy the boundary condition that their derivatives are zero on the boundary between the inner and outer regions, i.e., $[df_{il_is}(r_2)/dr_2]_{r_2=a}=0$. These functions are eventually continued to the outer-region functions $F_{il_i}(r_2)$ in Eq. (2). The configurations ϕ_k decay before they reach the boundary. Some of them include occupied and unoccupied bound core orbitals of σ type, and others include approximate π virtual orbitals represented by a single-ζ basis function. The first sum in Eq. (3) and some of the terms in the second sum together constitute a converged two- (electronic) state close-coupling wave function. Other terms in the second sum represent correlation effects. In reality the terms in Eq. (3) are rearranged by constructing orthonormal σ orbitals in terms of the bound σ orbitals and the continuum basis functions. The π virtual orbitals need not be accurate for the present purpose, because they are used merely to construct correlation terms to allow for short-range polarization of the core ion. The Hamiltonian matrix defined over the inner region and constructed with the configurations in Eq. (3) is then diagonalized.

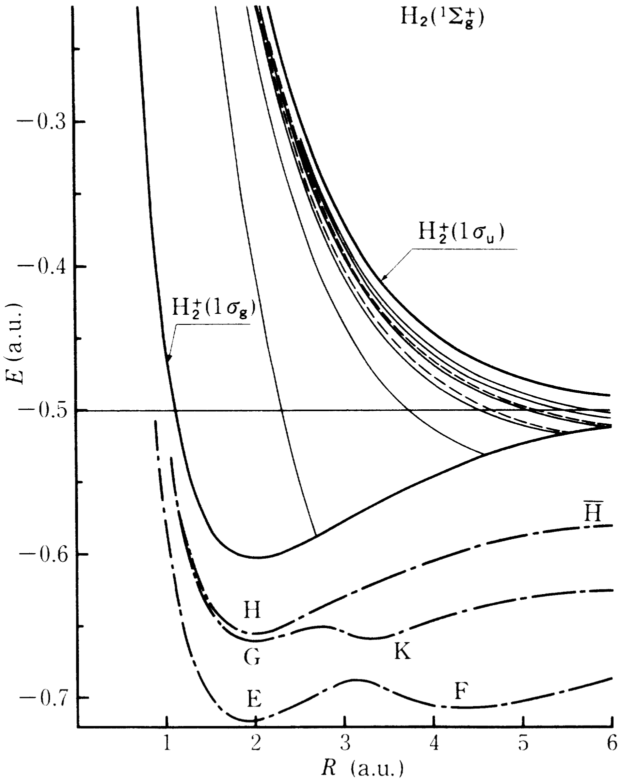

FIG. 1. Potential-energy curves of the two lowest states of H_2^+ and doubly excited states of H_2. The energy is the total energy including the nuclear repulsion term. Solid curves: H_2^+. Thin curves: six lowest members of the series $H_2(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$. Dashed curves: two lowest members of the series $H_2(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$. (See Table V for higher members.) Dot-dashed curves: bound states of H_2.

We define the $\underline{R}$ matrix by

$$F_{il_i}(a) = \sum_{j,l_j} R_{il_i,jl_j}(E;a) \left[r_2 \frac{dF_{jl_j}(r_2)}{dr_2} \right]_{r_2=a} \qquad (4)$$

in terms of the channel wave functions $F_{il_i}(r_2)$ of the Rydberg electron. Each element of the $\underline{R}$ matrix is calculable from the eigenvalues $E_p^{(\underline{R})}$ and the eigenvectors $\mathbf{c}_p$ of the modified Hamiltonian matrix as[36,38–40]

$$R_{il_i,jl_j}(E;a) = \frac{1}{2a} \sum_p \frac{w_{il_ip} w_{jl_jp}}{E_p^{(\underline{R})} - E} \qquad (5)$$

with

$$w_{il_ip} = \sum_s f_{il_is}(a) c_{p,il_is} \ . \qquad (6)$$

To correct this $\underline{R}$ matrix approximately for the functional space disregarded in Eq. (3), we apply the method proposed by Buttle.[42]

In the outer region the wave function (2) is substituted into the Schrödinger equation. This leads to six coupled second-order ordinary differential equations. They are numerically solved using the $\underline{R}$-matrix propagation method[43] from the boundary $r_2=a$, starting with the boundary condition (4), out to a certain point of r_2. From there on, the Gailitis expansion method[44] is used to obtain the asymptotic form of the solutions, and hence the $\underline{K}$ matrix. It is then diagonalized and the eigenphase sum $\delta(E)$ is calculated. We repeat these calculations

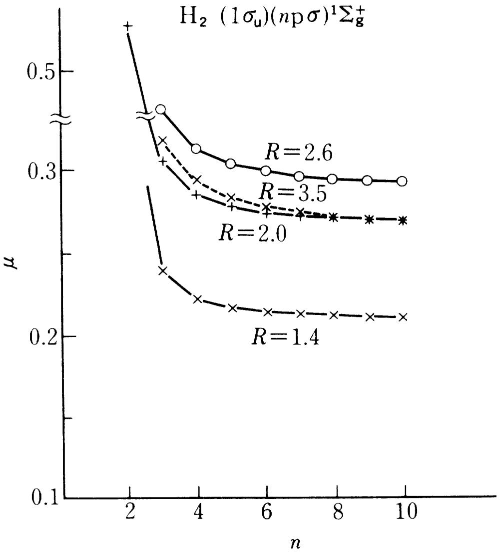

FIG. 2. The real part μ of the quantum defect of the $H_2(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$ state as a function of the principal quantum number n. R is the internuclear distance in atomic units.

TABLE III. The total energies $E(n)$, the energies $E_r(n)$ above the ground state of $H_2{}^+$, and the energy widths $\Gamma(n)$ of the three lowest doubly excited states of $H_2({}^1\Sigma_g^+)$ compared with the results of bound-state–type calculations covering a wide range of the internuclear distance R. The correct energy of $H_2{}^+(X\,{}^2\Sigma_g^+)$ has been used to calculate $E(n)$ from the present results of $E_r(n)$. All quantities are given in atomic units. Numbers in curly brackets are energies of diabatically extrapolated states.

		Present			Present			Present		Hazi[a]		Guberman[b]		Lesech[c]
R	$E_r(2)$	$E(2)$	$\Gamma(2)$	$E_r(3)$	$E(3)$	$\Gamma(3)$	$E_r(4)$	$E(4)$	$\Gamma(4)$	$E(2)$	$\Gamma(2)$	$E(2)$	$E(3)$	$E(3)$
1.0	0.7003	0.2485	1.50[−2][d]	0.8228	0.3711	2.57[−3]	0.8520	0.4002				0.2434	0.3569	
1.2	0.5802	0.0512	2.07[−2]	0.7086	0.1796	3.01[−3]	0.7384	0.2094	1.30[−3]			0.0483	0.1812	0.175
1.4	0.4705	−0.0994	2.76[−2]	0.6058	0.0359	3.58[−3]	0.6364	0.0664	1.45[−3]	−0.102	2.5[−2]	−0.1016	0.0360	0.032
1.6	0.3715	−0.2194	3.52[−2]	0.5148	−0.0762	4.13[−3]	0.5461	−0.0449	1.62[−3]	[−0.211]		−0.2208	−0.0761	−0.079
1.8	0.2828	−0.3174	4.31[−2]	0.4349	−0.1654	4.58[−3]	0.4669	−0.1333	1.77[−3]	[−0.314]		−0.3175	−0.1652	−0.168
2.0	0.2042	−0.3985	5.09[−2]	0.3655	−0.2372	4.96[−3]	0.3981	−0.2045	1.89[−3]	−0.399	4.8[−2]	−0.3969	−0.2369	−0.239
2.2	0.1348	−0.4660	5.85[−2]	0.3054	−0.2954	5.26[−3]	0.3386	−0.2623	2.00[−3]	[−0.463]				−0.298
2.4	0.0732	−0.5233	6.52[−2]	0.2538	−0.3428	5.52[−3]	0.2872	−0.3093	2.10[−3]	[−0.519]				
2.5	0.0452	−0.5486	6.76[−2]	0.2307	−0.3631	5.64[−3]	0.2643	−0.3295	2.15[−3]	−0.545	6.4[−2]	−0.5404	−0.3629	
2.6	0.0191	−0.5717	6.98[−2]	0.2093	−0.3815	5.77[−3]	0.2430	−0.3478	2.20[−3]	[−0.569]				−0.385
2.80				0.1711	−0.4133	6.01[−3]	0.2049	−0.3795	2.33[−3]	{[−0.614]}				
3.00				0.1383	−0.4393	6.23[−3]	0.1720	−0.4056	2.46[−3]	{−0.651}		{−0.6307}	−0.4395	−0.444
3.25				0.1037	−0.4653	6.49[−3]	0.1372	−0.4319	2.63[−3]	{[−0.675]}				
3.40										{[−0.685]}				−0.485
3.50				0.0752	−0.4856	6.81[−3]	0.1083	−0.4526	2.82[−3]	{[−0.689]}				
3.75				0.0518	−0.5014	7.14[−3]	0.0842	−0.4689	3.06[−3]	{[−0.698]}				
4.00				0.0325	−0.5136	7.42[−3]	0.0642	−0.4818	3.36[−3]	{−0.702}		{−0.7257}	−0.5168	−0.525
4.25				0.0166	−0.5230	7.58[−3]	0.0477	−0.4920	3.72[−3]					
4.40														−0.542
4.50				0.0037	−0.5302	7.69[−3]	0.0341	−0.4998	4.33[−3]					
4.75							0.0236	−0.5053	5.57[−3]					
5.00							0.0129	−0.5115						{−0.560}

[a] Hazi *et al.* (Ref. 31). Includes the energy shift. Numbers in parentheses have been recovered from a figure in Ref. 31.

[b] Guberman (Ref. 33). Projection-operator *QHQ* formalism without energy shift.

[c] Lesech and Aubert-Frécon (Ref. 34). Prolate-spheroidal wave-function method without energy shift.

[d] $1.50[-2]=1.50\times10^{-2}$.

TABLE IV. Stabilization points R_c in atomic units for dissociation of superexcited states $H_2(1\sigma_u)(nl\sigma)\,^1\Sigma_g^+$.

State	Present	HDB[a]	HS[b]
$(1\sigma_u)^2$	2.68	2.65	2.53
$(1\sigma_u)(3p\sigma)$	4.58		
$(1\sigma_u)(4p\sigma)$	5.5		
$(1\sigma_u)(4f\sigma)$	5.6		

[a] Hazi *et al.* (Ref. 31).

[b] Hara and Sato (Ref. 32).

changing the energy E, and search for an abrupt increase of $\delta(E)$ by π, corresponding to a resonance. The shape of the resonant behavior of $\delta(E)$ is fitted to the Breit-Wigner formula,[45] and the complex energies of doubly excited Rydberg states are determined.

To search for very narrow resonances, say, of the order of 10^{-6} Ry, we have to repeat the calculations for energies E at extremely fine intervals. In fact, this is easily accomplished and does not involve much computer time, once the eigenvalues and the eigenvectors of the modified

TABLE V. Complex quantum defects $\mu(n)+i\gamma(n)$ of doubly excited Rydberg states of $H_2(^1\Sigma_g^+)$. R, internuclear distance; $4.30[-2]=4.30\times10^{-2}$.

$R=1.2$ a.u.

	$(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$		$(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$	
n	$\mu(n)$	$\gamma(n)$	$\mu(n)$	$\gamma(n)$
2	0.391	4.30[−2]		
3	0.215	3.26[−2]		
4	0.200	3.56[−2]	−0.0114	7.90[−5]
5	0.196	3.87[−2]	−0.0116	1.68[−4]
6	0.195	4.14[−2]	−0.0116	2.59[−4]
7	0.194	4.38[−2]	−0.0116	3.43[−4]
8	0.193	4.57[−2]	−0.0116	4.18[−4]
9	0.193	4.73[−2]	−0.0116	4.83[−4]
10	0.192	4.85[−2]	−0.0116	5.37[−4]

$R=1.4$ a.u.

	$(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$		$(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$	
n	$\mu(n)$	$\gamma(n)$	$\mu(n)$	$\gamma(n)$
2	0.425	5.39[−2]		
3	0.240	3.76[−2]		
4	0.224	3.90[−2]	−0.0096	8.37[−5]
5	0.218	4.00[−2]	−0.0099	1.40[−4]
6	0.215	4.08[−2]	−0.0101	1.78[−4]
7	0.214	4.13[−2]	−0.0101	2.04[−4]
8	0.213	4.17[−2]	−0.0102	2.23[−4]
9	0.213	4.19[−2]	−0.0102	2.37[−4]
10	0.212	4.21[−2]	−0.0102	2.47[−4]

$R=1.6$ a.u.

	$(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$		$(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$	
n	$\mu(n)$	$\gamma(n)$	$\mu(n)$	$\gamma(n)$
2	0.461	6.43[−2]		
3	0.266	4.22[−2]		
4	0.247	4.28[−2]	−0.0080	1.27[−4]
5	0.241	4.33[−2]	−0.0084	2.02[−4]
6	0.238	4.37[−2]	−0.0086	2.48[−4]
7	0.236	4.39[−2]	−0.0087	2.77[−4]
8	0.235	4.40[−2]	−0.0088	2.97[−4]
9	0.235	4.41[−2]	−0.0088	3.10[−4]
10	0.234	4.42[−2]	−0.0088	3.21[−4]

$R=1.8$ a.u.

	$(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$		$(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$	
n	$\mu(n)$	$\gamma(n)$	$\mu(n)$	$\gamma(n)$
2	0.498	7.34[−2]		
3	0.288	4.57[−2]		
4	0.268	4.60[−2]	−0.0067	2.03[−4]
5	0.262	4.62[−2]	−0.0071	3.20[−4]
6	0.258	4.63[−2]	−0.0073	3.88[−4]
7	0.256	4.64[−2]	−0.0074	4.30[−4]
8	0.255	4.65[−2]	−0.0075	4.59[−4]
9	0.254	4.66[−2]	−0.0076	4.78[−4]
10	0.254	4.66[−2]		

$R=2.0$ a.u.

	$(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$		$(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$	
n	$\mu(n)$	$\gamma(n)$	$\mu(n)$	$\gamma(n)$
2	0.533	8.08[−2]		
3	0.307	4.85[−2]		
4	0.286	4.85[−2]	−0.0055	3.29[−4]
5	0.278	4.85[−2]	−0.0060	5.11[−4]
6	0.275	4.86[−2]	−0.0063	6.16[−4]
7	0.273	4.87[−2]	−0.0064	6.81[−4]
8	0.271	4.87[−2]	−0.0065	7.24[−4]
9	0.270	4.88[−2]	−0.0066	7.54[−4]
10	0.270	4.88[−2]	−0.0067	7.75[−4]

$R=2.2$ a.u.

	$(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$		$(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$	
n	$\mu(n)$	$\gamma(n)$	$\mu(n)$	$\gamma(n)$
2	0.565	8.70[−2]		
3	0.321	5.06[−2]		
4	0.299	5.06[−2]	−0.0046	5.24[−4]
5	0.291	5.07[−2]	−0.0052	8.04[−4]
6	0.287	5.08[−2]	−0.0055	9.64[−4]
7	0.285	5.08[−2]	−0.0057	1.06[−3]
8	0.283	5.09[−2]	−0.0058	1.13[−3]
9	0.282	5.09[−2]	−0.0059	1.17[−3]
10	0.282	5.09[−2]	−0.0060	1.20[−3]

TABLE V. (*Continued*).

$R=2.4$ a.u.

	$(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$		$(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$	
n	$\mu(n)$	$\gamma(n)$	$\mu(n)$	$\gamma(n)$
2	0.597	9.09[−2]		
3	0.331	5.25[−2]		
4	0.308	5.28[−2]	−0.0039	8.18[−4]
5	0.299	5.30[−2]	−0.0047	1.24[−3]
6	0.295	5.31[−2]	−0.0050	1.48[−3]
7	0.292	5.32[−2]	−0.0052	1.62[−3]
8	0.291	5.32[−2]	−0.0054	1.72[−3]
9	0.290	5.32[−2]	−0.0055	1.79[−3]
10	0.289	5.33[−2]	−0.0055	1.84[−3]

$R=2.6$ a.u.

	$(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$		$(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$	
n	$\mu(n)$	$\gamma(n)$	$\mu(n)$	$\gamma(n)$
2	0.624	9.17[−2]		
3	0.337	5.45[−2]		
4	0.312	5.53[−2]	−0.0036	1.26[−3]
5	0.303	5.56[−2]	−0.0044	1.89[−3]
6	0.299	5.59[−2]	−0.0049	2.24[−3]
7	0.296	5.60[−2]	−0.0051	2.44[−3]
8	0.294	5.60[−2]	−0.0053	2.58[−3]
9	0.293	5.61[−2]	−0.0054	2.67[−3]
10	0.292	5.62[−2]	−0.0055	2.74[−3]

$R=2.8$ a.u.

	$(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$		$(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$	
n	$\mu(n)$	$\gamma(n)$	$\mu(n)$	$\gamma(n)$
2				
3	0.340	5.67[−2]		
4	0.314	5.83[−2]	−0.0036	1.91[−3]
5	0.304	5.89[−2]	−0.0046	2.82[−3]
6	0.299	5.92[−2]	−0.0051	3.31[−3]
7	0.296	5.94[−2]	−0.0054	3.65[−3]
8	0.294	5.95[−2]	−0.0055	3.79[−3]
9	0.293	5.95[−2]	−0.0057	3.92[−3]
10	0.293	5.97[−2]		

$R=3.0$ a.u.

	$(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$		$(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$	
n	$\mu(n)$	$\gamma(n)$	$\mu(n)$	$\gamma(n)$
2				
3	0.338	5.88[−2]		
4	0.312	6.18[−2]	−0.0039	2.83[−3]
5	0.301	6.29[−2]	−0.0050	4.13[−3]
6	0.296	6.35[−2]	−0.0056	4.81[−3]
7	0.293	6.37[−2]	−0.0059	5.18[−3]
8	0.291	6.39[−2]	−0.0060	5.48[−3]
9	0.290	6.41[−2]	−0.0062	5.64[−3]
10	0.289	6.42[−2]	−0.0063	5.76[−3]

$R=3.25$ a.u.

	$(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$		$(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$	
n	$\mu(n)$	$\gamma(n)$	$\mu(n)$	$\gamma(n)$
2				
3	0.331	6.17[−2]		
4	0.304	6.64[−2]	−0.0052	4.54[−3]
5	0.293	6.83[−2]	−0.0064	6.48[−3]
6	0.288	6.93[−2]	−0.0070	7.47[−3]
7	0.285	6.99[−2]	−0.0073	8.03[−3]
8	0.283	7.02[−2]	−0.0075	8.40[−3]
9	0.282	7.05[−2]	−0.0076	8.66[−3]
10	0.281	7.07[−2]		

$R=3.5$ a.u.

	$(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$		$(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$	
n	$\mu(n)$	$\gamma(n)$	$\mu(n)$	$\gamma(n)$
2				
3	0.317	6.58[−2]		
4	0.291	7.21[−2]	−0.0077	7.10[−3]
5	0.281	7.48[−2]	−0.0089	9.93[−3]
6	0.276	7.63[−2]	−0.0094	1.14[−2]
7	0.273	7.70[−2]	−0.0096	1.22[−2]
8	0.271	7.76[−2]	−0.0098	1.27[−2]
9	0.269	7.79[−2]	−0.0099	1.30[−2]
10				

$R=3.75$ a.u.

	$(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$		$(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$	
n	$\mu(n)$	$\gamma(n)$	$\mu(n)$	$\gamma(n)$
2				
3	0.299	7.04[−2]		
4	0.274	7.93[−2]	−0.0116	1.08[−2]
5	0.263	8.32[−2]	−0.0125	1.48[−2]
6	0.258	8.53[−2]	−0.0128	1.68[−2]
7	0.255	8.62[−2]	−0.0129	1.78[−2]
8	0.253	8.70[−2]	−0.0130	1.85[−2]
9	0.252	8.74[−2]	−0.0130	1.87[−2]
10	0.251	8.80[−2]		

$R=4.0$ a.u.

	$(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$		$(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$	
n	$\mu(n)$	$\gamma(n)$	$\mu(n)$	$\gamma(n)$
2				
3	0.278	7.50[−2]		
4	0.252	8.85[−2]	−0.0172	1.62[−2]
5	0.241	9.41[−2]	−0.0174	2.16[−2]
6	0.235	9.82[−2]	−0.0172	2.41[−2]
7	0.231	1.03[−1]	−0.0171	2.55[−2]
8	0.229	1.02[−1]	−0.0169	2.63[−2]
9				
10				

$R=4.25$ a.u.

	$(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$		$(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$	
n	$\mu(n)$	$\gamma(n)$	$\mu(n)$	$\gamma(n)$
2				
3	0.252	7.88[−2]		
4	0.225	1.00[−1]	−0.0246	2.35[−2]
5	0.211	1.11[−1]	−0.0234	3.08[−2]
6	0.202	1.20[−1]	−0.0225	3.39[−2]
7	0.193	1.35[−1]	−0.0218	3.55[−2]
8			−0.0213	3.67[−2]
9	0.185	1.39[−1]	−0.0208	3.73[−2]
10			−0.0207	3.72[−2]

Hamiltonian, which contains the detailed information on the H_2 system over the inner region, have been calculated. Since w and $E_p^{(\underline{R})}$ in Eq. (5) are both independent of E, they need to be calculated only once. The E-dependent Buttle correction for the $\underline{R}$ matrix is easily calculated, and the E-dependent outer-region coupled equations are solved extremely rapidly. Thus the $\underline{R}$-matrix method is particularly useful for our purpose not only from the physical point of view as stated in the beginning of this section but also from the computational viewpoint.

III. RESULTS

We have carried out calculations at some 30 internuclear distances R up to 5 a.u. adopting an inner-region radius a of 12 a.u. For large R we have also tried a larger inner region with $a = 16$ a.u. and have confirmed that the results are independent of the radius. For $R \leq 4$ a.u. many isolated resonances have been found for the first time above the previously known three resonances, as shown in Fig. 1, and are classified into two series, one of which is considerably narrower than the other. The three lowest resonances belong to the broader series. The energy position of each resonance satisfies the Rydberg formula with an effective principal quantum number n^* close to an integer. The broader series starts from a member with $n^* \simeq 2$ and the narrower series with $n^* \simeq 4$. We identify the former to be the $(1\sigma_u)(np\sigma)$ Rydberg series and the latter to be the $(1\sigma_u)(nf\sigma)$ series, though the lowest $np\sigma$ member has two electrons in the same molecular orbital and has little Rydberg character.

The three lowest $np\sigma$ resonances ($n = 2,3,4$) are fully discussed in the literature for $R \leq 2.6$ a.u.[4–7,30–34] Rather than repeating discussion of all previous calculations Table II briefly compares the positions of these resonances $E_r(n)$ above the ground state of H_2^+ and the energy widths $\Gamma(n)$ at $R = 2$ a.u. with previous calculations of close-coupling type.[4,5,7] Naturally, the results of previous $\underline{R}$-matrix calculations similar to the present ones are close to the present results.

Table III compares the results for the two lowest resonances with those of bound-state-type calculations carried out up to large internuclear distances.[31,33,34] Agreement among different calculations is seen to be good. In particular the results of Refs. 31 and 33 are close to the present results. Extrapolation of the resonance potential curves gives the crossing points R_c of these curves with the threshold of the continuum, i.e., with the potential curve of the ground state of H_2^+ (Fig. 1). These crossing points, which are included in Table IV, are important as the stabilization points of dissociative recombination through the lowest resonances. One of the dissociation fragments H from this process is in the ground state and the other is in an excited state that depends on the intermediate resonance state.

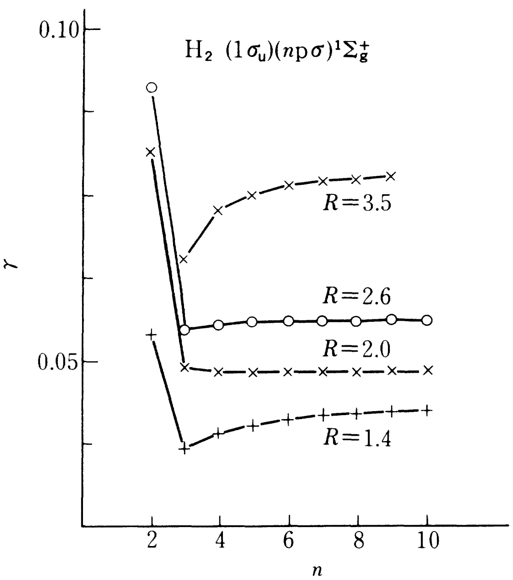

FIG. 3. The imaginary part γ of the quantum defect of the $H_2(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$ state as a function of the principal quantum number n. R is the internuclear distance in atomic units.

The complex quantum defect has been calculated from the resonance position and width for each Rydberg state and the results are given in Table V. Note that the real part μ is slightly different from what would be obtained from only the real part of the energy; see Eq. (1). Figures 2 and 3 show the quantum defect for $np\sigma$ series for some small values of R as functions of n. Both the real and imaginary parts approach smoothly and quickly the series limit values, and exemplify the usefulness of the complex quantum defect in characterizing doubly excited

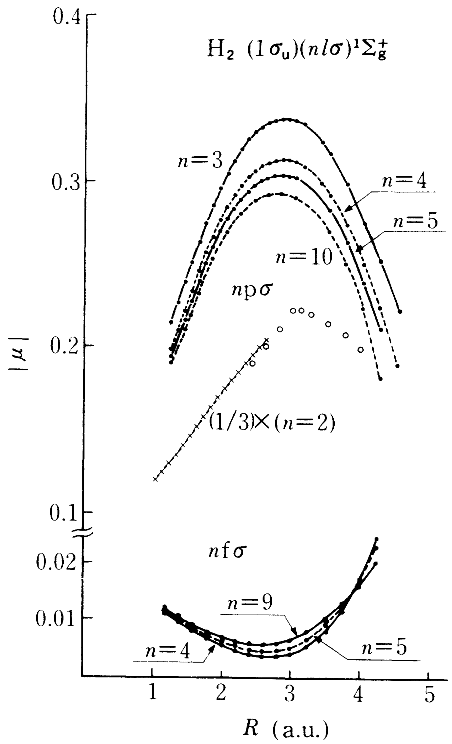

FIG. 4. The real part μ of the quantum defect of the $H_2(1\sigma_u)(nl\sigma)\,^1\Sigma_g^+$ state as a function of the internuclear distance R. Open circles: recovered from the figure of the diabatic potential curve $(1\sigma_u)^2$ in Ref. 31.

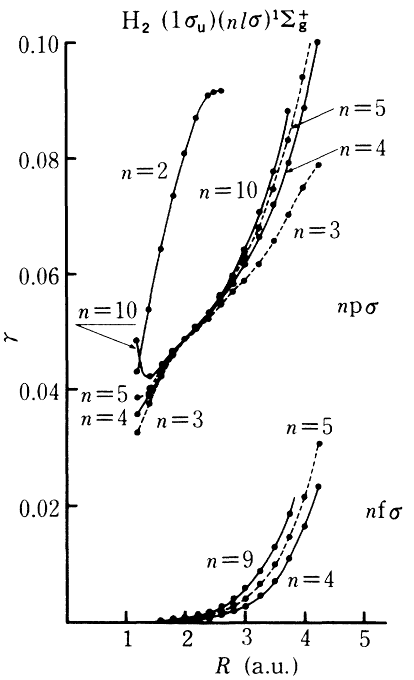

FIG. 5. The imaginary part γ of the quantum defect of the $H_2(1\sigma_u)(nl\sigma)\,^1\Sigma_g^+$ state as a function of the internuclear distance R.

Rydberg states. In particular, the imaginary part is quite stable for $n \geq 3$ for 2.0 a.u. $\leq R \leq 2.4$ a.u.

Figures 4 and 5 show the variation of the complex quantum defects for $np\sigma$ and $nf\sigma$ series with the internuclear distance. Both the real and imaginary parts of the quantum defect for $nf\sigma$ are much smaller than those for $np\sigma$. This is due to a weaker interaction between the ion core and the Rydberg electron with a higher angular momentum, i.e., with a higher potential barrier that prevents the electron from penetrating the inner region. The real part of the quantum defect for $np\sigma$ with $n \geq 3$ has a maximum around $R = 2.6$–2.8 a.u., whereas that for $nf\sigma$ has a minimum around there. On the other hand, the imaginary part continues to increase with R more rapidly for larger R for both the $np\sigma$ and $nf\sigma$ series. The lowest $np\sigma$ resonance, or the $(1\sigma_u)^2$ resonance, has little Rydberg character and appears to show a behavior quite different from that of other members in the series; the real part of the quantum defect keeps increasing with R up to the crossing point, and the imaginary part bends over as has been discussed previously.[5] If we use the results of the diabatic extrapolation of this resonance of Hazi *et al.* beyond the crossing point, as are included in Table III,[31] the real part of the quantum defect is seen to have a maximum around $R = 3.0$–3.2 a.u. in a manner similar to the higher members.

The upper members of the two Rydberg series begin to overlap each other for $R > 4$ a.u. where the energy of the series limit lies above the ground state of the H_2^+ core by only a small amount. There the two series mix with each other and the quantum defect (especially its imaginary part) behaves irregularly as a function of R and of n. Here we have an example of multichannel quantum defect theory of autoionizing Rydberg series with a single common series limit.

IV. CONCLUSION

We have applied the $\underline{R}$-matrix method for electron-molecule collisions to the doubly excited adiabatic Rydberg series $(1\sigma_u)(np\sigma)\,^1\Sigma_g^+$ and $(1\sigma_u)(nf\sigma)\,^1\Sigma_g^+$ of the hydrogen molecule. Unlike the only previous $\underline{R}$-matrix calculations of molecular Rydberg states (of CH),[46] we have obtained smoothly behaving complex quantum defects. Detailed calculations of doubly excited states of $H_2(^1\Sigma_g^+)$ reported in the literature are limited to three lowest members of the $(1\sigma_u)(np\sigma)$ series for the smaller internuclear distances. The present study has revealed the global feature of the Rydberg-state parameters along each series up to high n and as functions of R over a wide range. The results illustrate the usefulness of the $\underline{R}$-matrix method for dealing with doubly excited molecular Rydberg series and pave the way to accurate studies of other symmetries and higher-lying series of H_2, to extensions to many other molecules, and to studies of dynamic processes that occur via these superexcited states.

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