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Superexcited States of the Hydrogen Molecule Converging to the First Excited State of the Hydrogen Molecular Ion

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The Feshbach operator formalism was used to calculate thirty doubly excited states of the H_2 molecule of the symmetries $^1\Sigma_{g,u}^+$, $^1\Pi_{g,u}$, and $^1\Delta_{g,u}$ for internuclear distances up to 8 a.u. Basis functions involving Sonine polynomials and centered on either nucleus or on the center of nuclear mass allowed accurate inclusion of many one-electron molecular orbitals. Comparison is made with previous results in the literature.

KEYWORDS: atomic physics, molecule, superexcited state, autoionizing state, resonance

§1. Introduction

The literature on doubly excited states of the hydrogen molecule H_2 is abundant because it is the simplest molecular system with electron correlations. The doubly excited states of H_2 play a role of important intermediate states in many processes such as photoionization, photodissociation, and electron-impact ro-vibrational excitation and dissociative excitation/recombination.[1] In these processes the coupling between the electronic and nuclear motions can be essential in general, but is difficult to treat theoretically in a proper way. When a Franck-Condon transition is important, however, the adiabatic approximation is very useful. Even when the electronic-nuclear coupling is important, the adiabatic approximation is useful both for the physical understanding of the dynamic processes and as the basis of more sophisticated calculations.

Thus many calculations in the adiabatic approximation have been done on doubly excited states of H_2, which are examples of superexcited states. However, the knowledge of these superexcited states is still insufficient. Particularly, calculations of the higher states belonging to the series converging to the first excited state of the ion H_2^+, which are often called the Q_1 series, are scarce. Furthermore, the knowledge of the states belonging to the series converging to the second (Q_2 series) or a higher excited state of H_2^+ is far from sufficient. The continuum processes involving these Q_2 and higher superexcited states seem to have never been calculated properly.

An early attempt of bound-state-type calculations of the energies of doubly excited Q_1 states of H_2 and Fermi-golden-rule calculations of their widths was made by Bottcher and Docken[2] for $^1\Sigma_g^+$, $^3\Sigma_u^+$, and $^3\Pi_g$ symmetries for internuclear distances R up to 2.5 a.u. More sophisticated calculations of the resonance parameters became available later: Collins and collaborators,[3-6] Hazi[7] and Hazi *et al.*,[8] and Hara and Sato[9] and Sato and Hara,[10] to name a few. The variational scattering-type calculation by Takagi and Nakamura[11] used a trial function involving spheroidal functions. Guberman[12] carried out bound-state-type calculations of one or two Q_1 states of each of the $^{1,3}\Sigma_{g,u}^+$ and $^{1,3}\Pi_{g,u}$ symmetries for R up to 6 a.u. The R-matrix method was then applied to the calculations of doubly excited Q_1 states by, *e.g.*, Tennyson and Noble[13] and Shimamura *et al.*[1] This work was recently greatly expanded by Tennyson.[14] More recent calculations of the lowest five Q_1 states of each of the $^{1,3}\Sigma_{g,u}^+$, $^{1,3}\Pi_{g,u}$, and $^{1,3}\Delta_{g,u}$ symmetries for $0 \leq R \leq 5$ a.u. by Sánchez and Martín[15] use the Feshbach projection operator formalism with B-spline functions for an L^2 description of the nonresonant continuum. More extensive lists of references are found in Tennyson[14] and Sánchez and Martín.[15]

In the present work we attempt to develop a computational method useful and efficient for even more extensive calculations of high-lying members of the Q_1 series and even the Q_2 series. For this purpose we first choose a set of basis functions that are centered either on one of the nuclei or on the center of mass and that include Sonine polynomials rather than simple Slater-type or Gaussian-type orbitals. Each subset consisting of basis functions with a common center is a set of orthogonal functions. This choice of basis functions leads to highly accurate energies of the molecular ion H_2^+ up to very highly excited electronic states. These states are then used for constructing many configurations for the CI-type calculations of both low-lying and high-lying doubly excited H_2 states using the Feshbach projection operator. The accuracy of this method is demonstrated for thirty doubly excited Q_1 states of the symmetries $^1\Sigma_{g,u}^+$, $^1\Pi_{g,u}$, and $^1\Delta_{g,u}$ for R up to 8 a.u.

§2. Computational Method

2.1 Analytic wave functions for H_2^+

We wish to use analytic trial functions for the calcu-

lations of adiabatic doubly excited H_2 states written as linear combinations of Slater determinants. For this purpose we first write approximate bound electronic states of H_2^+ as linear combinations of a finite number of analytic basis functions, although adiabatic electronic states of H_2^+ can be represented exactly by the sum of known infinite series of functions.[16] Since we are trying to calculate highly excited H_2 states, we need many highly excited H_2^+ wave functions. The usual two-center expansion of these wave functions is inappropriate for highly excited states, which are not localized around the positions of the nuclei. The two-center expansion would lead to the necessity of inclusion of many terms in the expansion, and, in turn, to the difficulty of linear dependence.

Therefore, we use a three-center expansion method. In other words, we use three types of basis functions $\varphi_{Nlm}(\mathbf{r}_s)$, $s = a, b, c$, each centered on nucleus a or nucleus b, or on the center of mass c. Also, we replace the usual Slater-type or Gaussian-type orbitals by functions

$$\varphi_{Nlm}(\mathbf{r}_s) = (2\alpha r_s)^l L_N^{2l+2}(2\alpha r_s)\exp(-\alpha r_s)Y_{lm}(\hat{\mathbf{r}}_s), \tag{2.1}$$

involving Sonine polynomials $L_N^{2l+2}(x)$ (or associated Laguerre polynomials to within a multiplicative constant). Here, Y_{lm} is a spherical harmonic, N is the order of the Sonine polynomial, and α is a variational parameter, although we did not fully optimize it in actual calculations. We tried a few sets of values of α and chose a convenient and reasonable set; convergence with respect to the size of the basis set was confirmed.

The functions $\varphi_{Nlm}(\mathbf{r}_s)$ $(N = 0, 1, 2, \cdots)$ contain a polynomial $\sum_{i=l}^{l+N} c_i r_s^i$ and are similar to the hydrogen-like wave functions $(2\alpha_n r_s)^l L_{n-l-1}^{2l+1}(2\alpha_n r_s)\exp(-\alpha_n r_s) \times Y_{lm}(\hat{\mathbf{r}}_s)$ $(n - l - 1 = 0, 1, 2, \cdots)$, where it is to be noted that $\alpha_n = Z/n$ (with Z the effective charge) depends on the order of the Sonine polynomial. The set of functions $\{\varphi_{Nlm}(\mathbf{r}_s)\}_{Nlm}$ with a common center s and with a common value of α is a set of orthogonal functions. This choice of basis functions is seen later to avoid the difficulty of overcompleteness.

The wave functions $\Psi_{im_i}(\mathbf{r})$ $(i = 1, 2, 3, \cdots)$ of H_2^+ are written in terms of eq. (2.1) as

$$\Psi_{im_i}(\mathbf{r}) = \sum_{s=a,b,c}\sum_{N,l} C_{Nl}^{(s)}\varphi_{Nlm_i}(\mathbf{r}_s), \tag{2.2}$$

where the coefficients $C_{Nl}^{(s)}$ are determined by diagonalizing the Hamiltonian matrix for H_2^+.

The types of basis functions used in the actual calculations are summarized in Table I. There, the values of l and α are tabulated together with the center s of the coordinate; a±b stands for the functions $\varphi_{Nlm_i}(\mathbf{r}_a) \pm \varphi_{Nlm_i}(\mathbf{r}_b)$. Note that all basis functions centered on the center of mass c are more diffuse than the tightest basis function centered on the nuclei a and b. This choice was made since the higher-lying states are considered to have a large component of basis functions on c and since the lower-lying states are considered to have a large component of basis functions on a and b. This was confirmed by examining the wave functions actually calculated.

The chosen range of the values of N is also included in the table. The use of all the basis functions in Table I leads to the size of the basis set 189 for σ_g, 168 for σ_u, 148 for π_g, 182 for π_u, 182 for δ_g, and 186 for δ_u.

The calculated electronic energies of the $1\sigma_g$ $(1s\sigma)$, $10\sigma_g$ $(6d\sigma)$, $1\sigma_u$ $(2p\sigma)$, and $10\sigma_u$ $(7p\sigma)$ states are tabulated together with the quantum defects in Table II as examples and are compared with exact values calculated using a code of Power.[16] Very accurate results are seen

Table I. Types of basis functions for H_2^+ used in the present calculation. See text for the notation.

σ_g			σ_u			π_g		
	$N = 0 \sim 20$			$N = 0 \sim 20$			$N = 0 \sim 20$	
s	l	α	s	l	α	s	l	α
a+b	0	2.0	a−b	0	1.5	a−b	1	1.5
c	0	0.5	a+b	1	0.5	a+b	2	0.5
a−b	1	2.0	c	1	0.5	c	2	0.5
a+b	2	2.0	a−b	2	0.5	c	4	0.5
c	2	0.5	c	3	0.5	c	6	0.5
c	4	0.5	c	5	0.5	c	8	0.5
c	6	0.5	c	7	0.5	c	10	0.5
c	8	0.5	c	9	0.5			
c	10	0.5						
π_u			δ_g			δ_u		
	$N = 0 \sim 25$			$N = 0 \sim 25$			$N = 0 \sim 20$	
s	l	α	s	l	α	s	l	α
a+b	1	1.5	a+b	2	1.0	a−b	2	1.0
c	1	0.5	c	2	0.5	a+b	3	0.5
c	3	0.5	c	4	0.5	c	3	0.5
c	5	0.5	c	6	0.5	c	5	0.5
c	7	0.5	c	8	0.5	c	7	0.5
c	9	0.5	c	10	0.5	c	9	0.5
c	11	0.5	c	12	0.5	c	11	0.5
						c	13	0.5

to have been obtained. A similar comparison for all the symmetries $\sigma_{g,u}$, $\pi_{g,u}$, and $\delta_{g,u}$ has revealed an accuracy of the present quantum defects higher than $\sim 10^{-7}$ radians for both low-lying and high-lying H_2^+ states up to the twentieth state for each symmetry, indicating that the set of basis functions used in this calculation is large enough for the present purpose.

2.2 *Wave functions for H_2*

The neutral hydrogen wave functions $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ are expanded in terms of Slater determinants consisting of the electronic states of H_2^+ calculated in the preceding subsecion. Singly excited states of H_2 were first calculated as a test of the basis set. Some examples are compared in Table III with accurate literature values.[17,18] The agreement is seen to be satisfactory.

Table II. The electronic energies E_{elec} and the quantum defects μ of some states of H_2^+ calculated by the basis-function method, as compared with exact values calculated by the code of Power.[16] R: internuclear distance.

	R (a.u.)	E_{elec} (a.u.)			μ		
		Basis func.	Exact	Error	Basis func.	Exact	Error
	0.5	−1.734987910	−1.734988000	9.0E−8			
	0.8	−1.554480027	−1.554480094	6.7E−8			
	1.0	−1.451786282	−1.451786313	3.1E−8			
	1.4	−1.284269240	−1.284269242	2.1E−9			
$1\sigma_g$	2.0	−1.102634210	−1.102634214	4.3E−9			
$(1s\sigma)$	3.0	−0.9108961932	−0.9108961974	4.2E−9			
	4.0	−0.7960848822	−0.7960848837	1.5E−9			
	6.0	−0.6786357148	−0.6786357151	2.7E−10			
	8.0	−0.6275703882	−0.6275703886	4.0E−10			
	0.5	−0.05564506353	−0.05564506359	6.3E−11	0.0048275978	0.0048276012	3.4E−9
	0.8	−0.05578998787	−0.05578998804	1.7E−10	0.0126194206	0.0126194297	9.1E−9
	1.0	−0.05592944735	−0.05592944750	1.5E−10	0.0200888147	0.0200888225	7.8E−9
	1.4	−0.05632708623	−0.05632708630	6.9E−11	0.0412336740	0.0412336776	3.6E−9
$10\sigma_g$	2.0	−0.05727743745	−0.05727743750	5.3E−11	0.0908745787	0.0908745815	2.8E−9
$(6d\sigma)$	3.0	−0.05973766975	−0.05973767855	8.8E−9	0.2138343994	0.2138348258	4.3E−7
	4.0	−0.06198005133	−0.06198005137	3.9E−11	0.3194677206	0.3194677224	1.8E−9
	6.0	−0.06300090218	−0.06300090408	1.9E−9	0.3656786445	0.3656787293	8.5E−8
	8.0	−0.06183729639	−0.06183729924	2.9E−9	0.3129145834	0.3129147145	1.3E−7
	0.5	−0.5168854595	−0.5168854652	5.7E−9			
	0.8	−0.5427459121	−0.5427459207	8.6E−9			
	1.0	−0.5648136170	−0.5648136251	8.1E−9			
	1.4	−0.6120799716	−0.6120799764	4.8E−9			
$1\sigma_u$	2.0	−0.6675343897	−0.6675343922	2.5E−9			
$(2p\sigma)$	3.0	−0.7014183325	−0.7014183334	8.6E−10			
	4.0	−0.6955506390	−0.6955506394	4.4E−10			
	6.0	−0.6573105590	−0.6573105590	4.2E−11			
	8.0	−0.6236060155	−0.6236060156	1.0E−10			
	0.5	−0.04119286866	−0.04119286880	1.4E−10	0.0320667882	0.0320668003	1.2E−8
	0.8	−0.04169665877	−0.04169665896	1.9E−10	0.0742889211	0.0742889368	1.6E−8
	1.0	−0.04205554153	−0.04205554167	1.4E−10	0.1039026595	0.1039026711	1.2E−8
	1.4	−0.04261256233	−0.04261256243	9.6E−11	0.1491229565	0.1491229642	7.7E−9
$10\sigma_u$	2.0	−0.04286728579	−0.04286728586	7.3E−11	0.1695077222	0.1695077281	5.8E−9
$(7p\sigma)$	3.0	−0.04238096556	−0.04238096560	4.5E−11	0.1304296666	0.1304296702	3.6E−9
	4.0	−0.04152939496	−0.04152939499	3.5E−11	0.0603559371	0.0603559400	2.9E−9
	6.0	−0.03973194969	−0.03973194972	2.7E−11	−0.0948800818	−0.0948800794	2.4E−9
	8.0	−0.03810936606	−0.03810936620	1.4E−10	−0.2443451818	−0.2443451687	1.3E−8

Table III. Calculated energies (in a.u.) of singly excited states of H_2 compared with previous calculations. R: Internuclear distance in a.u.

State	R	E_{elec} Present	E_{elec} Literature	Difference
$2^1\Sigma_g^+$	2.0	−0.71334	−0.71770[a]	0.00436
$3^1\Sigma_g^+$	2.0	−0.66018	−0.66036[a]	0.00018
$4^1\Sigma_g^+$	2.0	−0.65341	−0.65439[a]	0.00098
$1^1\Pi_u$	1.4	−0.68434	−0.68833[b]	0.00399
$2^1\Pi_u$	1.4	−0.62217	−0.62337[b]	0.00120
$3^1\Pi_u$	1.4	−0.60129	−0.60112[b]	−0.00018
$4^1\Pi_u$	1.4	−0.59974	−0.60023[b]	0.00049

a) Wolniewicz and Dressler.[17]
b) Rothenberg and Davidson.[18]

For the calculation of doubly excited states converging to the first excited state of H_2^+, we obtain eigenvalues of the Hamiltonian H of the H_2 molecule projected onto the subspace defined by the projection operator

$$Q(1,2) = Q(1)Q(2), \tag{2.3}$$

where

$$Q(i) = 1 - P(i) = 1 - |1\sigma_g(i)\rangle\langle 1\sigma_g(i)|. \tag{2.4}$$

In other words, we project out the $1\sigma_g$ orbital of either electron. Since we are using a set of orthogonal H_2^+ wave functions, we have only to remove the configurations involving the $1\sigma_g$ orbital.

We investigated the convergence of the energies of the doubly excited states as the number of configurations is increased. We confirmed that the energies converged to enough number of significant figures when we used all ten lowest H_2^+ states of each symmetry to construct the H_2 configurations. The total number of configurations used in the calculations of the eigenvalues of $Q(1,2)HQ(1,2)$ range from 330 to 400 depending on the symmetry. Inclusion of additional basis functions in Table I, *e.g.*, two-center basis functions with larger angular momenta, naturally did not change the H_2 results at least within six significant figures.

Guberman[12] has also done similar $Q(1,2)HQ(1,2)$ calculations with H_2 configurations constructed from H_2^+ wave functions. However, our H_2^+ wave functions in terms of improved set of basis functions are much more accurate than his, and also the number of configurations in our calculations is larger than his; he used some tens of configurations. Guberman calculated only one or two doubly excited states of each symmetry, whereas we are particularly interested in higher lying doubly excited states and therefore we need a larger number of configurations involving higher H_2^+ states.

§3. Results and Discussion

Figures 1–6 show calculated electronic energies (excluding the internuclear Coulomb repulsion) of the lowest five doubly excited states of H_2 of the symmetries ${}^1\Sigma_{g,u}^+$, ${}^1\Pi_{g,u}$, and ${}^1\Delta_{g,u}$ for the internuclear distances R up to 8 a.u.; tabulated energies are available from the author upon request.

Figures 1–6 also include the results of Sánchez and Martín[15] for comparison. The general trend of the R behavior of the electronic energies agrees well between the present results and those of Sánchez and Martín. However, there is a general tendency that their electronic energies get larger than ours for R larger than about 3 or 4 a.u. The avoided crossings between some doubly excited states found at small R by Sánchez and Martín were confirmed by the present calculations, although the absolute values of the energies to the left of the crossings were sometimes not reproduced. The reason for the discrepancy is unknown. Comparison of the present results with other authors' calculations is found below in the text rather than in the figures to avoid complicated figures.

As was discussed by Sánchez and Martín,[15] the electronic energies of doubly excited states of H_2 approach those of He in the small R limit. Except in the small-R region the electronic energies except for the lowest ${}^1\Sigma_g^+$ energy are nearly parallel to the first excited state of H_2^+, suggesting their Rydberg nature. At large distances these doubly excited states become bound eventually since the two lowest H_2^+ energies merge eventually. Because of the projection operator $Q(1,2)$ these doubly excited bound states have a significance of diabatic states, and hence, they are included in Figs. 1–6. Their energies cross many true adiabatic-state energies and merge with singly excited states at large R.

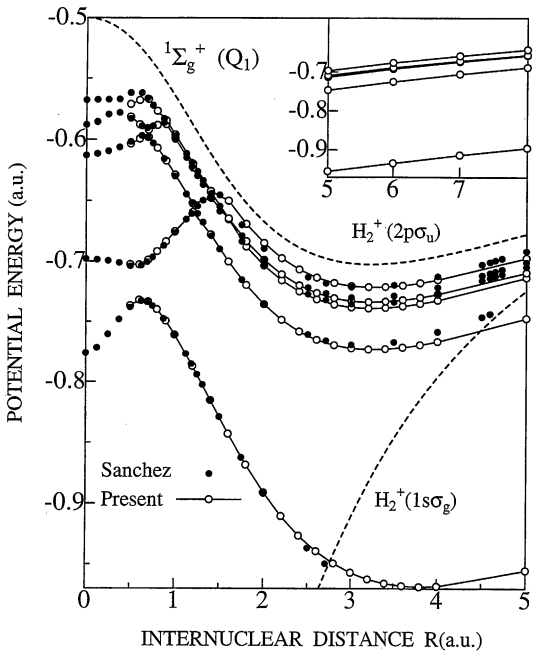

Fig. 1. Calculated electronic energies (open circles with solid curve) of the lowest five doubly excited states of H_2 of the ${}^1\Sigma_g^+$ symmetry compared with the results of Sánchez and Martín[15] (solid circles). The lowest two states of H_2^+ are shown by dashed curves. The third and fourth doubly excited states are indistinguishable in the inset.

3.1 ${}^1\Sigma_g^+(i)$ states

The dominant configuration for each of these states is discussed by Sánchez and Martín[15] in the region of R where they are autoionizing states; it is $2p\sigma_u 2p\sigma_u$ for $i=1$, $2p\sigma_u 3p\sigma_u$ for $i=2$, $2p\sigma_u 4f\sigma_u$ for $i=3$, $2p\sigma_u 4p\sigma_u$ for $i=4$, and $2p\sigma_u 5f\sigma_u$ for $i=5$. The present calculation showed, however, that the main configuration is $2p\sigma_u 2p\sigma_u$ for $i=1$, $2p\sigma_u 4p\sigma_u$ for $i=2$, $2p\sigma_u 5p\sigma_u$ for $i=3$, $2p\sigma_u 5f\sigma_u$ for $i=4$, and $2p\sigma_u 6p\sigma_u$ for $i=5$. By studying the coefficients of various configurations, we found that $2p\sigma_u 3p\sigma_u$ is not the dominant one for any autoionizing state, although it mixes strongly in the first and/or second state. A further, careful examination of our wave functions reveals a strong mixing between configurations $2p\sigma_u i\sigma_u$ and $2p\sigma_u j\sigma_u$ if the orbitals $i\sigma_u$ and $j\sigma_u$ have the same united-atom angular momentum. A similar trend was found for all other symmetries, where two configurations with the second electron having the same united-atom angular momentum are strongly mixed with each other.

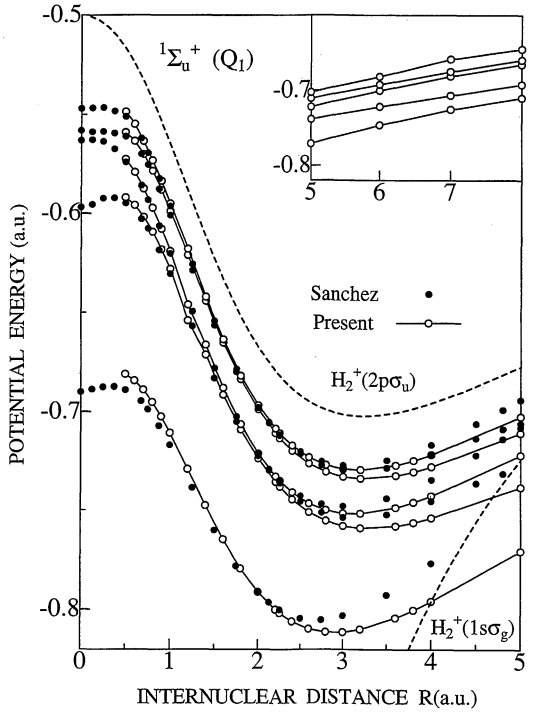

Fig. 2. Calculated electronic energies (open circles with solid curve) of the lowest five doubly excited states of H_2 of the $^1\Sigma_u^+$ symmetry compared with the results of Sánchez and Martín[15] (solid circles). The lowest two states of H_2^+ are shown by dashed curves.

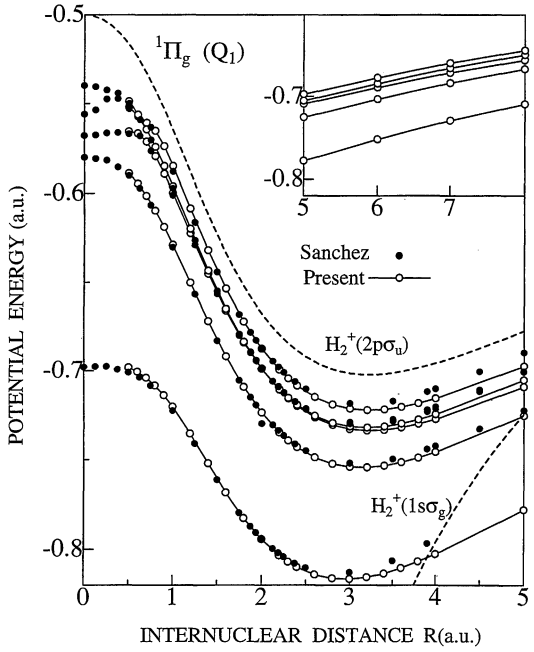

Fig. 3. Calculated electronic energies (open circles with solid curve) of the lowest five doubly excited states of H_2 of the $^1\Pi_g$ symmetry compared with the results of Sánchez and Martín[15] (solid circles). The lowest two states of H_2^+ are shown by dashed curves. The third and fourth doubly excited states are indistinguishable in the region 1 a.u.$<R<$3 a.u.

Tracing the change in the coefficients of the main configurations as R changes, we found that the main configurations are sometimes switched into different states in the region of bound states. This can be easily understood as due to crossings with true adiabatic bound states.

Our electronic energy for the lowest doubly excited state $^1\Sigma_g^+(1)$ is a little higher, especially at large R, than Guberman's energy.[12] Our values are also a little higher than the results obtained by some other authors, *e.g.*, the R-matrix calculations by Shimamura *et al.*[1] and Tennyson,[14] at the larger R. This could be due to our use of the projection operator that projects out the $1\sigma_g$ orbital, and to the coupling with continuum taken into account in these R-matrix calculations.

3.2 $^1\Sigma_u^+(i)$ *states*

The dominant configurations for $i = 1$–5, according to the present calculation, are $2p\sigma_u 2s\sigma_g$, $2p\sigma_u 4d\sigma_g$, $2p\sigma_u 4s\sigma_g$, $2p\sigma_u 5d\sigma_g$, and $2p\sigma_u 5s\sigma_g$, respectively, for intermediate values of R, although avoided crossings occur at smaller R between closely spaced pair of levels $i = 2$ and 3 and also $i = 4$ and 5, and these avoided crossings interchange the dominant configurations. The configurations $2p\sigma_u 3s\sigma_g$ and $2p\sigma_u 3d\sigma_g$ are not the dominant ones in any state, although they mix strongly in the lowest three autoionizing states. In the region of bound states the main configurations are sometimes switched into different states, just like in the case of the $^1\Sigma_g^+$ states.

Guberman's energy of the state $^1\Sigma_u^+(1)$ agrees well with the present result. However, his $^1\Sigma_u^+(2)$ state seems to correspond to our $^1\Sigma_u^+(3)$ state (although the energies of these two states begin to disagree with each other for R larger than 2.0 a.u.). This must be due to his neglect of the configuration $2p\sigma_u 4d\sigma_g$, which is the main configuration in $^1\Sigma_u^+(2)$. The energy of the state $^1\Sigma_u^+(1)$ calculated by Takagi and Nakamura[11] agrees well with the present result up to $R = 2.2$ a.u. Their $^1\Sigma_u^+(2)$ energy is a little higher than ours for R beyond 1.8 a.u. Tennyson's results[14] for $^1\Sigma_u^+(1,2)$ agree well with ours for R less than 4.0 a.u.

3.3 $^1\Pi_g(i)$ *states*

The dominant configurations for $i = 1$–5 were found to be $2p\sigma_u 2p\pi_u$, $2p\sigma_u 4p\pi_u$, $2p\sigma_u 5p\pi_u$, $2p\sigma_u 5f\pi_u$, and $2p\sigma_u 6f\pi_u$, respectively, for $R = 1.0$ and 2.0 a.u., although the third and fourth states interchange the dominant configuration by the time R becomes 4.0 a.u. The configuration $2p\sigma_u 3p\pi_u$ is not the main one in any state, but is mixed strongly in the first and second states. Also, the configuration $2p\sigma_u 4f\pi_u$ mixes strongly with $2p\sigma_u 5f\pi_u$ but the latter is always the main configuration.

Guberman's energy of the state $^1\Pi_g(1)$ agrees fairly well with the present result. However, his $^1\Pi_g(2)$ state deviates from ours for R larger than 4.0 a.u. This is considered to be due to his neglect of the configuration $2p\sigma_u 4p\pi_u$, which is the main configuration in $^1\Pi_g(2)$. Our results on $^1\Sigma_u^+(1)$ agree with Sato and Hara[10] but are slightly lower than those by Collins and Schneider.[3]

3.4 $^1\Pi_u(i)$ *states*

The main configuration for each of the lowest five states was found to be $2p\sigma_u 4d\pi_g$, $2p\sigma_u 5d\pi_g$, $2p\sigma_u 6g\pi_g$,

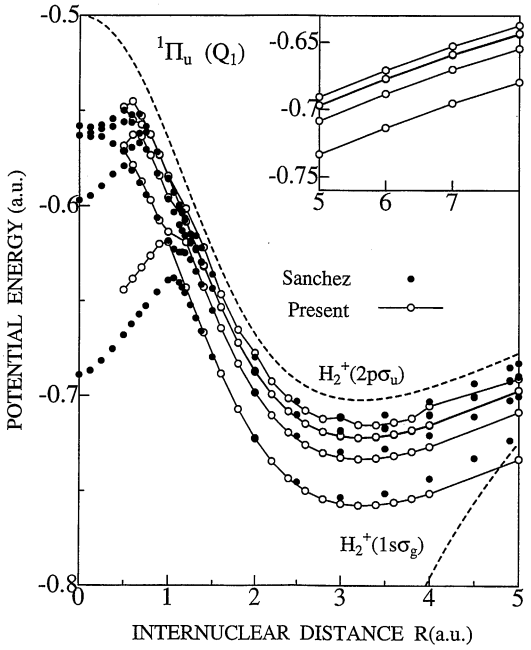

Fig. 4. Calculated electronic energies (open circles with solid curve) of the lowest five doubly excited states of H_2 of the $^1\Pi_u$ symmetry compared with the results of Sánchez and Martín[15] (solid circles). The lowest two states of H_2^+ are shown by dashed curves. The third and fourth doubly excited states are indistinguishable.

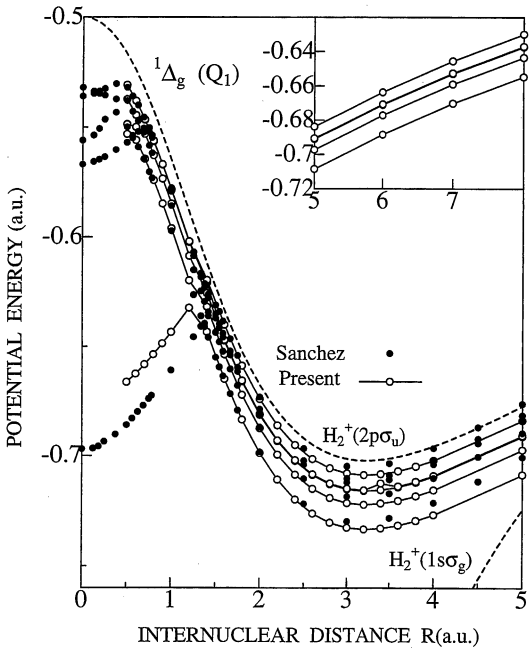

Fig. 5. Calculated electronic energies (open circles with solid curve) of the lowest five doubly excited states of H_2 of the $^1\Delta_g$ symmetry compared with the results of Sánchez and Martín[15] (solid circles). The lowest two states of H_2^+ are shown by dashed curves. The third and fourth doubly excited states are indistinguishable.

$2p\sigma_u 6d\pi_g$, and $2p\sigma_u 7g\pi_g$ for all the R values studied, although the second main configuration has a fairly large coefficient for all these states except for the second. Especially, the configuration $2p\sigma_u 3d\pi_g$ has a large component in $^1\Pi_u(1)$, and $2p\sigma_u 7d\pi_g$ is also important in $^1\Pi_u(4)$.

Guberman's energies for $i = 1$ and 2 are slightly higher than the present ones for 1.0 a.u.$<R<$6.0 a.u. His $^1\Pi_u(2)$ value at $R = 1.0$ a.u. corresponds to our $^1\Pi_u(3)$ state. Tennyson's results[14] on $i = 1$ and 2 are in generally good agreement with ours, except that his results do not show an avoided crossing that both the present work and Sánchez and Martín found around $R = 1.0$ a.u.

3.5 $^1\Delta_{g,u}(i)$ states

The main configurations for $^1\Delta_g(1\text{–}5)$ are $2p\sigma_u 5f\delta_u$, $2p\sigma_u 6f\delta_u$, $2p\sigma_u 7i\delta_u$, $2p\sigma_u 8f\delta_u$, and $2p\sigma_u 8i\delta_u$, respectively, for all the R values studied, and those for $^1\Delta_u(1\text{–}5)$ are $2p\sigma_u 3d\delta_g$, $2p\sigma_u 5d\delta_g$, $2p\sigma_u 6d\delta_g$, $2p\sigma_u 6g\delta_g$, $2p\sigma_u 7g\delta_g$, for the smaller R values, although the third and fourth states interchange the dominant configuration by the time R becomes 4.0 a.u. For both the gerade and the ungerade states the second main configuration has a large coefficient for all these states. For example, the configuration $2p\sigma_u 4f\delta_u$ mixes strongly into the lowest gerade state and $2p\sigma_u 4d\delta_g$ into the lowest ungerade state.

Sato and Hara[10] report the energy of the $^1\Delta_g(1)$ state that is considerably lower than the present results. Tennyson's results on $^1\Delta_{g,u}(1,2)$ are in fairly good agreement with the present results, but his results do not show an avoided crossing that both the present work and Sánchez and Martín found around $R = 1.2$ a.u.

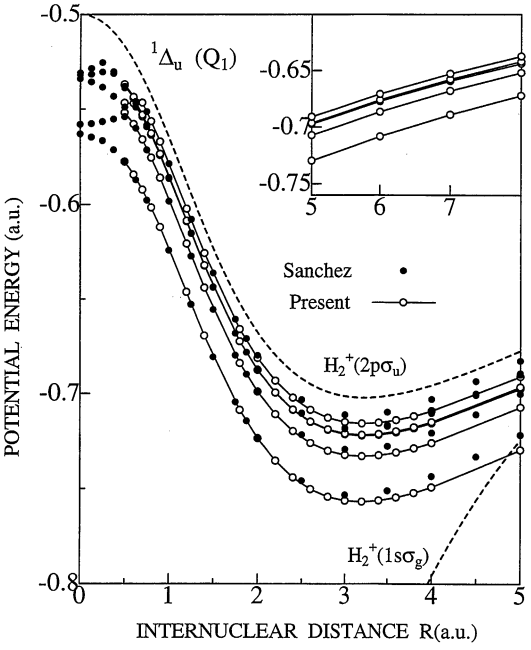

Fig. 6. Calculated electronic energies (open circles with solid curve) of the lowest five doubly excited states of H_2 of the $^1\Delta_u$ symmetry compared with the results of Sánchez and Martín[15] (solid circles). The lowest two states of H_2^+ are shown by dashed curves. The third and fourth doubly excited states are indistinguishable.

§4. Conclusion

We have developed a numerical method of three-center calculations of many high-lying doubly excited states of H_2, using a set of basis functions involving Sonine polynomials. Numerical examples have been reported for

thirty Q_1 states for a wide range of the internuclear distances, and the reliability of the method has been confirmed by comparison with existing data where available. This method has a prospect of being efficient for calculations of Q_2 and higher states, which would be the subject of future publications.

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