Interaction between two excited hydrogen atoms at large separations

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An investigation of the interaction between two excited hydrogen atoms yields the asymptotic forms of the doubly-excited states and terms of the H_2 molecule for large internuclear separations R. The leading term in the interaction energy is proportional to R^{-3} (dipole–dipole interaction). Because of the high degree of degeneracy of the unperturbed problem, the determination of the corresponding coefficients requires the solution of the secular problem. To lower the dimensionality of the latter problem and classify the states, specific symmetry properties of the system are analyzed. The interaction between the atoms in the lowest excited state is discussed in detail, and the energy terms $\sim R^{-5}$ (quadrupole–quadrupole interaction) for these states are found. The autoionization decay widths ($\sim R^{-6}$) for the quasimolecule states are computed, and the cross section for the Penning process $H^* + H^* \rightarrow H + H^+ + e$ is estimated.

§1. INTRODUCTION

Systems with one and two electrons are being actively studied in atomic physics both because of their practical importance and as fundamental standard problems. Two-electron systems, in particular, provide the simplest instance of the manifestation of an important effect: interelectron correlations. It is well known that, in the case of the helium atom, the correlations are strongest in the doubly excited states (see, for example, Refs. 1 and 2). The doubly excited states of the hydrogen molecule have received much less attention than those of the helium atom, although they have been the subject of a significant number of papers in the last few years (see, for example, Refs. 3 and 4). In particular, as far as we know, there has to date not been any investigation of the problem of the interaction of two excited hydrogen atoms, a problem which determines the behavior at large internuclear distances of the electronic terms of the hydrogen molecule that correspond to the doubly excited states. From the fundamental standpoint that problem is interesting in that, because of the additional degeneracy of the excited states of the hydrogen atom in the two-electron problem, the motions of the electrons are, generally speaking, strongly correlated even at large internuclear separations R. This is manifested in the form of the correct zeroth-order perturbation theory wave functions obtained through the diagonalization[1)] of the interelectron interaction operator in the basis of the degenerate states of the separated atoms (§3). In the multipole expansion of the latter operator for large R, the leading term is the dipole–dipole term, which governs the behavior of the terms in this limit ($\sim R^{-3}$). As is well known (see, for example, Ref. 5), such a dependence is characteristic of the interaction between identical atoms in different states with orbital angular momenta differing by unity. Physically, it is due to the excitation exchange between such atoms. In the case of hydrogen atoms the terms again behave like R^{-3} in the interaction of atoms with the same excitation energy. This is due to the additional degeneracy of the hydrogen levels and the possible existence of nonrelativistic hydrogen atoms in states with nonzero dipole moments.

The correlation of the electrons manifests itself also in the instability of the doubly excited states to autoionization. The asymptotic values of the autoionization widths are proportional to R^{-6}, and can also be computed (§4). The behavior of the terms of the quasimolecule at large R directly determines the cross section for a process like the Penning ionization $H^* + H^* \rightarrow H + H^+ + e$, as well as the cross sections for $(H^* + H^*)$-collision induced changes in the atomic orbital angular momentum and its orientation. Of even greater importance, apparently, is the fact that the doubly excited states of the H_2 molecule are easily excited radiatively or in collisions with fast charged particles. The separation of the nuclei along the corresponding doubly-excited terms leads to the production of excited hydrogen (H^*) atoms (if the autoionization-induced decay does not occur first) or H^* ions (if the autoionization process occurs). Such processes have been observed in numerous experimental investigations.[6] The published theoretical term calculations pertain to the region of medium R values, and practically do not consider the passage to the limit of separated atoms. The results obtained in the present paper should be useful for the passage to this limit and the construction of the correlation diagrams for the doubly excited states.

§2. THE EXACT AND APPROXIMATE SYMMETRY OF THE STATES

The exact quantum numbers for a diatomic molecule in the fixed-nuclei approximation are well known: these are the component Λ of the total orbital angular momentum along the internuclear axis, the total spin S, and also (for homonuclear molecules) the electron-coordinate inversion symmetry, indicated by the indices g and u,[5] at the center of the molecule. Accordingly, the states and terms of the molecule are denoted by the symbols $^{2s+1}\Lambda_{u,g}$. For the Σ states we must also indicate the symmetry with respect to reflection in

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the plane passing through the internuclear axis (the $\Sigma^{\pm}$ states). Because of the high degree of degeneracy of the energy levels of the excited hydrogen atom, there are, generally speaking, several terms of the same symmetry that go over, as $R \to \infty$, into a given energy level of the separated atoms. Therefore, for a more detailed classification of the states, it is desirable to have additional (exact or approximate) quantum numbers.

As the unperturbed Hamiltonian for two interacting hydrogen atoms, let us choose

$$H_0 = -{}^1/_2\nabla_1{}^2 - {}^1/_2\nabla_2{}^2 - 1/r_{1a} - 1/r_{2b}. \tag{1}$$

For neutral atoms the leading term in the interaction potential for $R \to \infty$ is the dipole–dipole interaction:

$$V_{d\text{-}d} = [\mathbf{r}_{1a}\mathbf{r}_{2b} - 3(\mathbf{r}_{1a}\mathbf{n})(\mathbf{r}_{2b}\mathbf{n})]/R^3, \quad \mathbf{n} = \mathbf{R}/R. \tag{2}$$

Here the vector $\mathbf{R}$ joins the atomic nuclei, $\mathbf{r}_{ja((b)}$ is the radius vector of the jth electron with respect to the nucleus $a(b)$ (in this paper we use the atomic system of units). Neither H_0, nor the perturbation possesses electron-interchange and inversion symmetries. Nonsymmetric perturbation theory is dealt with in sufficient detail in the literature (see, for example, Ref. 7). The present paper is devoted to the computation of the asymptotic power-law forms of the terms and their widths, quantities which can be calculated with the unsymmetrized—with respect to electron interchange—wave functions. After this, the eigenfunctions obtained can be symmetrized, and we can then assign them all the exact quantum numbers: in the process the terms acquire exponentially small (in the large R) corrections, which are not computed in the present paper.

Let us choose the unperturbed basis wave functions in the form

$$|(n_1n_2)l_1l_2m_1m_2\pm\rangle = [2(1+\delta_{n_1n_2}\delta_{l_1l_2}\delta_{m_1m_2})]^{-1/2} \times[\psi_{n_1l_1m_1}(r_{1a})\psi_{n_2l_2m_2}(r_{2b}) \pm\psi_{n_1l_1m_1}(r_{2b})\psi_{n_2l_2m_2}(r_{1a})], \tag{3}$$

where the ψ_{nlm} are the ordinary hydrogen-atom wave functions with spherical-harmonics quantum numbers l and m (as the axis of quantization, we have chosen the internuclear axis $\mathbf{n}$) and principal quantum number n. The functions (3) correspond to $\Lambda = m_1 + m_2$, do not (as discussed above) have definite spin and parity values, and correspond, as $R \to \infty$, to the energy $E_0 = -(n_1^{-2} + n_2^{-2})/2$.

The symmetrization or antisymmetrization of the basis states (3) with respect to electron interchange automatically yields the state with definite inversion symmetry (i.e., with a definite u or g symbol), specifically, the symmetrized states ($^1\Lambda$, $\Lambda = m_1 + m_2$) upon inversion acquire the factor $\pm(-1)^{l_1+l_2}$, while the antisymmetrized states ($^3\Lambda$) acquire the factor $\pm(-1)^{l_1+l_2+1}$.

The perturbation operator V_{d-d} (as well as the unperturbed Hamiltonian) is invariant under the transformation $\mathbf{r}_{1a} \to -\mathbf{r}_{1a}$, $\mathbf{r}_{2b} \to \mathbf{r}_{2b}$ (which, for brevity, is denoted below by P_0). This allows us to introduce an additional approximate quantum number: P_0 parity, which is "good" in the approximation (2) for the interaction. Notice that P_0 parity can be called an "inner parity" of the interacting atoms. the basis states (3) possess definite P_0 parity, equal to $(-1)^{l_1+l_2}$.

The operators H_0 and V_{d-d} are also symmetric under the transformation $\mathbf{r}_{1a} \to \mathbf{r}_{2b}$, $\mathbf{r}_{2b} \to \mathbf{r}_{1a}$, and this allows us to introduce another quantum number, which we shall call S_0 parity. The basis functions already possess definite S_0 parity, which is equal to ± 1, depending on the sign in (3).

Another symmetry operation that is important for the analysis of the properties of the spectrum is the transformation $\mathbf{r}_{1a} \to \mathbf{r}_{1a}$, $\mathbf{r}_{2b} \to \mathbf{r}_{2b}$, which is denoted below by P_1. The operator P_1 commutes with the unperturbed Hamiltonian (1), and anticommutes with the interaction operator (2):

$$\{V_{d\text{-}d},\ P_1\} = V_{d\text{-}d}P_1 + P_1V_{d\text{-}d} = 0. \tag{4}$$

It therefore follows that, if in the dipole-dipole interaction approximation some state ψ_I of the molecule corresponds to an energy shift $E_I \neq 0$ relative to the unperturbed ($R \to \infty$) position, then the state $P_I\psi_I$ is also an eigenstate, and corresponds to the energy shift $-E_I$. The eigenstates for which the energy shift in the dipole-dipole approximation is equal to zero possess definite P_1 parity.

For the P_0-odd states, the basis function (3) contains P_1-even and P_1-odd terms. The operator P_1 transforms the functions (3) with the indices + and − into each other. All the states form here pairs for which the level shifts in the dipole approximation differ in sign. The P_0-even basis functions possess a definite P_1 parity as well. Let there be i such functions with the same P_1 parity and j functions with opposite P_1 parity (for a fixed index + or − in (3) and a given Λ), and let $i > j$. Then there are i-j states for which the shift in the dipole aproximation is equal to zero. The remaining $2j$ states form pairs, in each of which the level shifts in the dipole approximation differ in sign.

Notice that, for the analysis of the properties of the operator V_{d-d}, the two-center character of the problem is practically unimportant, i.e., the vectors $\mathbf{r}_{1a}$ and $\mathbf{r}_{2b}$ can be considered to be measured from one and the same center. Thus, the problem coincides with the single-center problem (the helium atom), in which the electron-electron interaction has the form of the dipole-dipole interaction (and does not possess spherical symmetry).

To conclude this section, let us point out that, in the subspace of the states with given principal-quantum-number values n_1 and n_2, we can, in the case when $n_1 = n_2$, write the dipole-dipole interaction operator in terms of the integrals of motion for free hydrogen atoms, i.e., the Runge-Lenz electron operators $\mathbf{A}_{1a}$ and $\mathbf{A}_{2b}$:

$$V_{d\text{-}d} = 9n_1n_2\{\mathbf{A}_{1a}\mathbf{A}_{2b} - 3(\mathbf{A}_{1a}\mathbf{n})(\mathbf{A}_{2b}\mathbf{n})\}/4R^3. \tag{5}$$

[We have used here the identity

$$\mathbf{r}_i = -3n_i\mathbf{A}_i/2Z_i, \tag{6}$$

which is valid in the subspace of the states with a given n_i (Ref. 8)]. Then it is natural to raise the question whether we cannot construct from the operators $\mathbf{A}_i$ and $\mathbf{l}_i$ another operator that commutes with (5) (cf. the similarly formulated problem in the search for the approximate integrals of motion for the helium atom[9]). Such operators could not be found on the class of linear and bilinear combinations of the components of the vectors $\mathbf{A}_i$ and $\mathbf{l}_i$.

§3. THE TERMS AND STATES OF THE QUASIMOLECULE

The leading term in the asymptotic form of the terms of a quasimolecule composed of two excited hydrogen atoms is, in the general case, proportional to R^{-3}. The determination of the corresponding coefficient requires the diagonalization of the perturbation operator (2) or (5) (for $n_1 = n_2$) in the subspace of states with given n_1 and n_2, it being possible to achieve a significant reduction in the dimension of the matrix by taking into account the symmetry properties discussed in §2 above.[2)] We considered all the states with n_1, $n_2 \leqslant 3$. The energy level shifts for the most important case $(n_1,n_2) = (2,2)$ are given in Table I, where besides the standard designations of the states we also indicate their P_0 parities.

The role of the P_0-parity classification is apparent even in this simplest case. Indeed, let us first consider the Π states. It can be seen that there are, for example, two essentially different $^1\Pi_g$ states possessing different P_0 parities. The use of the last quantum number allows us to immediately write out the eignefunctions of the quasimolecule, and avoid the matrix-diagonalization procedure. A similar situation obtains for the other Π states.

The number of Σ states is the highest. In this case the P_0-odd states can be immediately separated, but there are among the P_0-even states triplets for which the other quantum numbers also coincide; here the perturbation matrix must be diagonalized. In this case, according to the general results that follow from the analysis of the P_1-parity operation, one energy level is unshifted, and the other two are located symmetrically with respect to it. The eigenfunctions of these states—two-electron orbitals (geminals) that take account of the correlation of the electrons—are superpositions of the basis functions, a fact which should be interpreted as the presence of strong interelectron correlations right up to extremely large internuclear distances. The nature of the indicated superpositions is such as to correspond to si-

TABLE I. Eigenfunctions, energies (up to the terms $\sim R^{-6}$), and autoionization widths of doubly excited states of the H_2 molecule that give hydrogen atoms in the first excited state upon separation of the nuclei.

Spectroscopic designation	P_0 parity	Eigenfunctions	Energy, a.u.	Width, a.u.
$^1\Delta_g$, $^3\Delta_u$	1	$\|(22)\ 1111+\rangle$	$\frac{216}{R^5}$	$\frac{1.504}{R^6}$
$^1\Pi_u$, $^3\Pi_g$	−1	$\|(22)\ 1010+\rangle$	$\frac{9}{R^3}$	$\frac{1.410}{R^6}$
$^1\Pi_g$, $^3\Pi_u$	−1	$\|(22)\ 1010-\rangle$	$\frac{-9}{R^3}$	$\frac{1.410}{R^6}$
$^1\Pi_g$, $^3\Pi_u$	1	$\|(22)\ 1110+\rangle$	$\frac{864}{R^5}$	$\frac{0.376}{R^6}$
$^1\Pi_u$, $^3\Pi_g$	1	$\|(22)\ 1110-\rangle$	0	$\frac{3.376}{R^6}$
$^1\Sigma_u^+$, Σ_g^+	−1	$\|(22)\ 1000+\rangle$	$\frac{-18}{R^3}$	$\frac{5.639}{R^6}$
$^1\Sigma_g^+$, $^3\Sigma_u^+$	−1	$\|(22)\ 1000-\rangle$	$\frac{+18}{R^3}$	$\frac{5.639}{R^6}$
$^1\Sigma_u^-$, $^3\Sigma_g^-$	1	$\|(22)\ 111-1-\rangle$	0	0
$^1\Sigma_g^+$, $^3\Sigma_u^+$	1	$\sqrt{\frac{2}{3}}\|(22)\ 111--1+\rangle$ $-\frac{1}{\sqrt{3}}\|(22)\ 1100+\rangle$	0	$\frac{3.008}{R^6}$
$^1\Sigma_g^+$, $^3\Sigma_u^+$	1	$-\frac{1}{\sqrt{2}}\|(22)\ 0000+\rangle$ $+\frac{1}{\sqrt{3}}\|(22)\ 1100+\rangle$ $+\frac{1}{\sqrt{6}}\|(22)\ 111-1+\rangle$	$\frac{9\sqrt{6}}{R^3}$ $+\frac{648}{R^5}$	$\frac{0.553}{R^6}$
$^1\Sigma_g^+$, $^3\Sigma_u^+$	1	$\frac{1}{\sqrt{2}}\|(22)\ 0000+\rangle$ $+\frac{1}{\sqrt{3}}\|(22)\ 1100+\rangle$ $+\frac{1}{\sqrt{6}}\|(22)\ 111-1+\rangle$	$-\frac{9\sqrt{6}}{R^3}$ $+\frac{648}{R^5}$	$\frac{0.553}{R^6}$

mulataneous changes in the orbital angular momentum and its component for each electron.

Notice that even the basis two-electron orbitals (3) include a certain amount of interelectron correlation, but this is of a more trivial kinematic nature.[3] A similar situation obtains in atomic theory, where the combination of the orbital angular momenta of electrons into a total angular momentum also implies the existence of some correlations. But normally the term correlations properly refers to the less trivial effects connected with the deviation from the Hartree-Fock approximation.

The calculations above show that there are a number of states for which the level shift in the dipole-dipole approximation vanishes. In these cases there naturally arises the question of which interaction gives the leading term in the asymptotic form of the term. Here, as follows from Table I, because of the symmetry properties, we do not need to solve the secular problem in the case $n_1 = n_2 = 2$; we just have to compute with the known wave functions the mean value for the corresponding interaction operator. The dipole-quadrupole interaction ($\sim R^{-4}$) anticommutes with the operator P_0, as a result of which all its diagonal matrix elements computed with functions of definite P_0 parity vanish. The next—in order of magnitude—interaction is the quadrupole-quadrupole interaction ($\sim R^{-5}$), the computations for which yield in a number of cases a nonzero shift[4] (see Table I). The dipole-octupole interaction, which has the same order of smallness in the asymptotic expansion, does not contribute to the matrix elements in the $n_1 = n_2 = 2$ case. But there are also terms to which the quadrupole-quadrupole interaction makes no contribution. The leading term in the asymptotic expression is given here by the dipole-dipole interaction in second order perturbation theory ($\sim R^{-6}$; the van der Waals potential). The calculation of the corresponding coefficient is beyond the scope of the present paper.

It can be seen from Table I that there are cases in which the asymptotic expressions for the term contains a nonzero term $\sim R^{-3}$, as well as nonzero terms $\sim R^{-5}$. The region of internuclear distances in which it is permissible to use the first term of the expansion can be estimated from the condition for equality of the first and second terms in order of magnitude, which yields $R \gtrsim 5.5 a_0$.

It can be seen from Table I that the term for the last of the considered states has a minimum at large internuclear separations. Using for the estimate the first two terms of the multipole expansion, we find that the minimum corresponds to the distance $R \approx 7 a_0$, and that it possesses quite a large depth (0.026 a.u.). Owing to the large value of R_0, such a molecular state is highly stable against autoionization (the width, as estimated from the results obtained in §4, is equal to 4×10^{-6} a.u., which is comparable to the radiative width).

In the $n_1 = n_2 = n$ case, the level shift for the state with the greatest possible value of $\Lambda (\Lambda = 2n - 2)$ is equal to zero in the dipole-dipole approximation for the interaction.

There are two states with $\Lambda = 2n - 3$; one of them is P_0 even, and for it the shift is also equal to zero on account of the selection rules. For the P_0-odd state the shift can be computed analytically:

$$\Delta E = \pm 9(n-1) n^2/4. \tag{7}$$

In the $n_1 = n_2 = 2$ case the structure of the spectrum is fully explained by the symmetry properties discussed in §2. But in the other cases, as the numerical computation shows, the spectrum possesses additional characterisitics, such as for instance degeneracy of some levels.

From the general point of view the subject of the present paper is the problem of the classification of the doubly excited states of the hydrogen molecule, i.e., the search for the complete set of quantum numbers for them. As has been shown, in certain cases it is sufficient for this purpose to add the quantum number P_0 to the standard quantum numbers entering into the designation ${}^{2S+1}\Lambda_{u,g}$ of the state, and also to the principal quantum numbers n_1 and n_2 of the separated atoms. In the general case it is also necessary to indicate the eigenvalue of the dipole-dipole operator to which the term in question corresponds.

If in addition we take the fine structure of the energy levels of the hydrogen atom into accout, then we can distinguish two asymptotic regions of internuclear separations according to the relation between the level splitting in the dipole-dipole approximation and the magnitude of the fine splitting; in the intermediate region there occurs a reconstruction of the states of the quasimolecule.

§4. THE AUTOIONIZATION WIDTHS AND THE PENNING PROCESS

As has already been indicated in the Introduction, a quasimolecule in the states under consideration is unstable against autoionization. The autoionization width in the simplest approximation is given by the well known perturbation theory formula:

$$\Gamma = 2\pi |\langle i | V | f \rangle|^2, \tag{8}$$

where $|i\rangle$ is the initial state (see §§ 2 and 3) and $|f\rangle$ is the final state in which one of the electrons is in the continuum and the other is in the hydrogen-atom state with the principal quantum number n_f. If n_1, $n_2 \geqslant 3$, then autoionization decay, the atom produced from which can either be in the ground state or in any of the excited ($n_f > 1$) states, is possible. The dominant contribution ($\sim R^{-6}$) to the width at large internuclear separations is made by the dipole–dipole term in the interaction V.

For the final state $|f\rangle$ the basis wave functions can be chosen in a form similar to (2):

$$|(n_f\varepsilon_0) l_f l_0 m_f m_0 \pm\rangle$$

$$= 2^{-1/2} [\psi_{n_f l_f m_f}(r_{1a}) \psi_{\varepsilon_0 l_0 m_0}(r_{2b}) \pm \psi_{n_f l_f m_f}(r_{2b}) \psi_{\varepsilon_0 l_0 m_0}(r_{1a})], \tag{9}$$

where $\psi_{\varepsilon_0 l_0 m_0}$ is the continuum Coulomb wave function normalized to the δ function of the electron energy. The quantity ε_0 can be found from the energy conservation law. In the general case the final states $|f\rangle$ should be constructed from the basis functions (9) in the same way as is done in §§ 2 and 3 for the initial states. But if we are interested not in the partial autoionization widths, but in the total width for the decay into a state with a given n_f, then we can use the formula

$$\Gamma_{nf}=2\pi\sum_{l_f,l_0,m_f,m_0}|\langle i|V_{d\text{-}d}|(n_f\varepsilon_0)l_fl_0m_fm_0\pm\rangle|^2, \qquad (10)$$

taking into account the fact that the matrix element

$$\langle(n_1n_2)l_1l_2m_1m_2|V_{d\text{-}d}|(n_f\varepsilon_0)l_fl_0m_fm_0\rangle$$

is nonzero only in the case when $l_1-l_f=\pm1$ and $l_2-l_0=\pm1$. Notice that the exact quantum numbers discussed in § 2 are conserved in autoionization.

Proceeding to the specific case of the states with $n_1=n_2=2$, let us note that here the only decay scheme possible is the one in which the hydrogen atom produced is in the ground state ($n_f=1$). For the ${}^1\Sigma_u^-$ and ${}^3\Sigma_g^-$ states the autoionization decay is strictly forbidden, since they are the lowest energy states with the appropriate symmetry. The results of the width calculations for the remaining states are given in Table I.

The results obtained can be directly used to estimate the cross section for the Penning process. In the case of sufficiently fast collisions we can consider the trajectories of the atomic particles to be rectilinear, and, ignoring the transitions between the the adiabatic states, estimate the cross section in the approximation first considered by Smirnov and Firsov[10] (see also Ref. 11). For slow collisions the curvature of the trajectories is important. In the simplest approximation the cross section for the Penning process can be assumed to be equal[11] to the orbit-formation cross section, which, for the interaction potential $V(R)=-\alpha/R^3$, has the form $\sigma=3\pi(\alpha/\mu v^2)^{3/2}$, where μ is the reduced mass and v is the collision velocity. To estimate the cross section, let us again ignore the transitions between the adiabatic states, and take into consideration the terms corresponding to attraction (both the R^{-3} and R^{-5} terms). For the cross section, averaged over the initial states, we obtain $\sigma=1300a_0^2$ for $v=(3kT/2\mu)^{1/2}$, $T=300$ K.

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[1)] To reduce the order of the matrix to be diagonalized, we must analyze the symmetry of the problem (§ 2).

[2)] Let us note that, in the case of the interaction between hydrogenlike ions, the degeneracy of the unperturbed states is partially lifted by the charge-dipole interaction ($\sim R^{-2}$).

[3)] The electron motions are least correlated in the wave functions used in the method of molecular orbitals, but, as is well known, this method is often inapplicable at large internuclear distances.

[4)] This same interaction is responsible for the next (after R^{-3}) term in the asymptotic expression for the remaining terms. This term is given in Table I.

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