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Autodetaching states of H_2^- and charge-transfer processes in H^- on H collisions

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A study is made of the $^2\Sigma_u^+$ and $^2\Sigma_g^+$ autodetaching states of H_2^- from the viewpoint of $H^- + H$, rather than the usual viewpoint of $e + H_2$. The model proposed in this work is a Feshbach-type formalism with two differences from previous studies. Guided by the structure of $H^- + H$ states at larger internuclear separations, Q space is defined by taking the singlet spin pair to be the pair of electrons on one center, rather than the pair of electrons in the lowest molecular orbital. These two specifications are the same at large separations, but depart from one another in the autodetaching region. It is suggested that such a Q space is more appropriate to the consideration of collisions of H^- on H than are the conventional H_2^- states obtained from the $e + H_2$ reaction. A second departure from previous works is the strengthening of the asymptotic condition on the Feshbach Q operator to require that $\langle p_r^2 + V(r) \rangle$ is less than zero for the diffuse electron, where $V(r)$ is the full Hartree-Fock potential produced by the core, including the Hartree-Fock parts of the $1/r_{ij}$ terms. This condition makes the diffuse electron unable to escape from the system unless it absorbs energy from the core or converts centrifugal motion into radial motion. Finally, it is shown that differential charge-exchange experiments for H^- on H can provide an experimental measurement of the energy difference between the $^2\Sigma_u^+$ and $^2\Sigma_g^+$ states and perhaps give some indication of their lifetimes as well.

I. INTRODUCTION

The hypothesis that H_2^- in one of its two energetically lowest resonance states is formed as an intermediate product during certain collision processes has been very fruitful.[1] It has permitted qualitative understanding of the essential aspects of three quite different collision reactions. In the first, a beam of low-energy electrons ($\leq$ 12 eV) is incident on a gas of H_2 molecules. The experimental results qualitatively explained in terms of H_2^- formation are (a) a sharp threshold peak in the dissociative attachment total cross sections at approximately 3.75 eV,[1-3] and a broader peak at approximately 10 eV,[4,5] (b) the angular distributions in dissociative attachment cross sections,[6,7] (c) the isotopic effect (when HD and D_2 are substituted for the H_2 targets) on the dissociative attachment total cross-sections,[2-5] (d) the noticeable effect on the dissociative attachment cross sections when the H_2 molecules are vibrationally and/or rotationally excited before the collision,[8,9] and (e) cross sections, total and differential in angle, for vibrational and rotational excitation of the H_2 target molecules.[7,10-15]

In the second reaction, a beam of H^- or D^- ions is incident on H or D target atoms in the energy range 0.01–2000 eV (100–10^7 K). The qualitative agreement between experimental and theoretical results is in the rate constant for the associative detachment reaction at ordinary temperatures[16-18] and in the total cross sections for electron detachment and for associative detachment.[19-21]

Finally, in the third reaction, a beam of D_2^+ is incident on cesium vapor at low keV energies. In this case, the theory has been able to predict a universal curve for the angular distribution of D^- dissociation fragments plotted in terms of reduced variables.[22]

Common to almost all the theoretical analyses which have led to understanding of the essential aspects of the experimental results has been the idea of the transient formation of one of the two lowest autodetaching states of H_2^-. This central idea of H_2^- formation as an intermediate complex during the collision has provided a satisfying physical picture of the phenomena involved in the three reactions. However, despite the successes, there are still serious problems that lead one to question this hypothesis. In general, quantitative agreement between theory and experiment has yet to be achieved. In particular, in the cross sections for vibrational and rotational excitation by electron impact, it appears that the nonresonant, or direct, contribution is as important as the resonant contribution.[23] There are, moreover, very different, sometimes even contradictory results from different reports of the effect on dissociative attachment of the initial vibrorotational excitation of the H_2 target molecule[8,9,24,25] and in

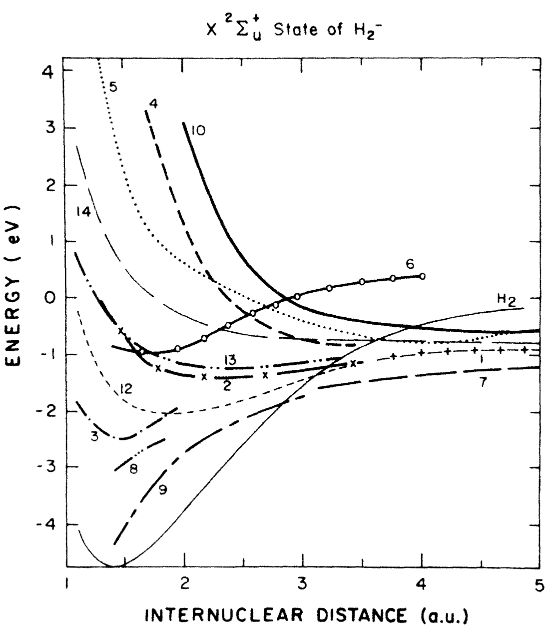

FIG. 1. Energy of the $X^2\Sigma_u^+$ state of H_2^-. The results of the present calculation are given by the heavy solid line, labeled 10. The legend for the energy curves is as follows: 1, Taylor and Harris (Ref. 30); 2, Bardsley, Herzenberg, and Mandl (Ref. 27); 3, Eliezer, Taylor, and Williams (Ref. 31); 4, Ostrovskii (Ref. 43); 5, Demiov and Ostrovskii (Ref. 41); 6, McCurdy and Mowrey (Ref. 29); 7, Senekowitsch *et al.* (Ref. 54); 8, Gauyacq (Ref. 52); 9, Gauyacq (Ref. 52); 10, present work; 12, Bardsley and Wadehra (Ref. 12); 13, Chen and Peacher (Ref. 3); 14, Mundel, Berman, and Domcke (Ref. 56). The H_2 ground-state energy, taken from Kolos and Wolniewicz (Ref. 55), is shown for comparison as the light solid line.

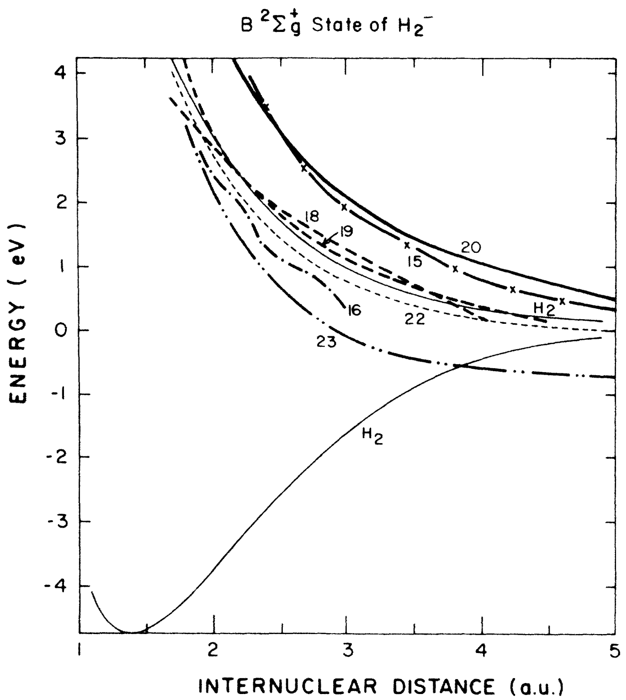

FIG. 2. Energy of the $B\,^2\Sigma_g^+$ state of H_2^-. The results of the present calculation are given by the heavy solid line labeled 20. The legend for the energy curves is as follows: 15, Bardsley, Herzenberg, and Mandl (Ref. 27); 16, Eliezer, Taylor, and Williams (Ref. 31); 18, Ostrovskii (Ref. 43); 19, Ostrovskii (Ref. 43); 20, present work; 22, Bardsley and Wadehra (Ref. 12); 23, Chen and Peacher (Ref. 3). The two lowest energy states of H_2, taken from Kolos and Wolniewicz (Ref. 55) are shown for comparison by the light solid lines.

dissociative attachment at collision energies less than 1 keV.[20,21,26,28] Most important, the calculated energy curves for the ground state of H_2^- obtained by different workers are spread over a wide energy range, as is shown in Figs. 1 and 2. The large discrepancies do not represent computational inaccuracies; rather, they represent differences in concept of what *is* the ground resonance state of H_2^-. Finally, there is still the question of the validity of thinking about a *molecular complex* (as opposed to an atomic state) that lives only 10^{-15} s.[9,23] There is thus no question about the need for further research on the lowest resonance states of H_2^- from both experimental and theoretical points of view.

Resonance states of negative ions have been classified into two categories, I and II. Resonance states of type I are characterized by being near to but below the energy of an excited state of the neutral system. On the other hand, resonance states of type II are characterized by being near to but above the energy of the ground or an excited state of the neutral system. The lowest resonant state of H_2^-, the $^2\Sigma_u$, is of type II, since Taylor and Harris[30] clearly established that it is in the continuum of the H_2 ground state. For the $^2\Sigma_g$ excites state of H_2^-, the situation is not so clear. Most of the theoretical results characterize it as a type-II resonance, but the results of Chen and Peacher,[3] Bardsley and Wadehra,[12] and Eliezer *et al.*[31] characterize it as a type-I resonance state.

The initial studies in H_2^- did not take into account that these resonance states are *not* eigenstates of the electronic Hamiltonian, and used variational techniques designed for the calculation of true eigenstates.[30,32] The difficulty with that approach is twofold. First, there are an infinite number of states of lower energy with the same symmetry, and they are not known. Second, the true continuum eigenstate of the Hamiltonian is the detached state; to obtain the resonance state, the Hamiltonian must be modified by means of projection operators, in order to obtain the localized transient state before autodetachment. These considerations are not merely in-principle arguments which can be ignored. In the initial studies, the basis sets used in the calculations grew in size and flexibility as time progressed, as did the number of configurations. As a consequence, the ground state of H_2^- decreased in energy as time progressed, approaching the energy of and resembling the wave function of the H_2 ground state more and more. Finally, in the most elaborate calculation,[30] both curves converged for distances less than $3a_0$, while the wave function of the loosely bound electron essentially described a free particle with zero kinetic energy. Clearly the lowest eigenstate of the electronic Hamiltonian for the three-electron system at interproton separations less than $3a_0$ is the H_2 ground state plus an electron at rest at infinity. In order to obtain the autodetaching states, the usual variational methods must be modified. The basic idea has been that these resonance states are very similar to some eigenstate for the neutral system to which a third electron is quasibound. Guided by this idea, the search has been limited to a region of Hilbert space. Additionally, some subsidiary condition is imposed on the wave function for the autodetaching electron. Three such approaches to autodetaching states of negative ions will be briefly described.

(1) Feshbach[33] proposed a very general theory of resonances, in which Hilbert space is divided into two subspaces by means of projection operators. The P subspace contains all the states energetically accessible to the system, known as open channels. It is possible to represent the resonances by means of linear superpositions of these states. The problem is reduced to solving a Schrödinger equation with an effective Hamiltonian in this subspace constructed by suppressing the closed channels. In favorable cases, the resonances are close to the eigenfunctions of QHQ, where Q denotes the projection operator complementary to P: Q space is complementary to P space. In practice, constructing the projection operators has become equated with the choice of a basic molecular structure together with a finite set of basis functions. A finite set of functions which behave as $r^n \exp(-\lambda r)$ satisfy the Feshbach asymptotic condition for Q subspace. However, as will be seen below, the use of such a projection operator does not automatically assure that the state thus found is the autodetaching state, rather than a poor approximation to the *detached* state. In general, the subspace must be carefully selected, since the basic physical assumptions of the model are incorporated into the definition of P and Q subspaces.

(2) Taylor and collaborators[34] proposed the so-called "stabilization method," which employs three fundamental criteria to determine the autodetaching state: (a) Election of some type of electronic structure as the most adequate to describe the state under study. Based on this structure, a function Ψ_{SCF} is found by a self-consistent-field calculation. In the process, an entire set of unoccupied orbitals is also produced. (b) Stabilization of the configuration-interaction wave function, Ψ_{CI}, with respect to the addition of more configurations. (c) Maximum localization of the wave packet that represents the autodetaching electron state by the selection of the function Ψ_{CI} that has maximum overlap with the function Ψ_{SCF}.

(3) Herzenberg and collaborators[35] have developed a different definition of the compound resonant state, based on the ideas of Kapur and Peierls[36] and Siegert.[37] This approach studies the singularities of the cross section which occur at certain complex values of the energy, when appropriate boundary conditions are imposed on the wave function over a surface which encloses the interaction region. Herzenberg and collaborators generalized this point of view to many-body and to atomic problems. In particular, they eliminate the unphysical S-matrix dependence on the radius r_0 defining the internal region. According to this group, a resonance is a solution to the Schrödinger equation for which the energy eigenvalue is complex and whose solution asymptotically approaches an outgoing wave. The imaginary part of the energy gives the lifetime of the compound state. They also propose a variational procedure to determine this solution.

It should also be mentioned that there exists yet another approach to autodetaching states which is not based on variational calculations.[38–43] The basic approximation consists of replacing the interaction between the diffuse electron and the core by a δ-function interaction with each core atom as a point object and assuming that the diffuse electron does not disturb the electronic structure of the core atoms. As a consequence, the action of the core atoms on the diffuse electron wave function is replaced by boundary conditions on the wave function at the locations of the core nuclei. Elsewhere, the diffuse electron is treated as a particle in a field-free region.

II. THE MODEL

In this paper, we focus our attention on the H_2^- resonance state from the viewpoint of a quasimolecular state in a collision between H^- and H. In the autodetaching region of internuclear separations, this is a linear combination of the ${}^2\Sigma_u$ ground resonance state and the ${}^2\Sigma_g$ excited resonance state. It is well known that for internuclear separations greater than a critical value R_0, which is very nearly $3a_0$, ground-state $H^- + H$ energy is below that of that for $H + H$. The respective energy curves cross at R_0. The $H^- + H$ system is thus stable at large internuclear separations and changes adiabatically as R decreases. We propose that there exists a diabatic $H^- + H$ state that continues into the autodetaching region. Demkov[38] differs from us in this latter consideration. He pictures the collision state in this internuclear region in terms of an electron instantly emitted into the continuum, the wave function of which is described by an expanding wave packet. As the two nuclei separate in the second half of the trajectory, the possibility of a bound state is reestablished, along with a finite probability of recapture of the outgoing electron. Our approach more resembles that of Herzenberg,[19] except that the uses potential curves obtained from the reaction $e + H_2$ in his analysis of the nuclear motion in the collision of H^- on H. Indeed, almost all the potential curves found in the literature for the two lowest states of H_2^- were tailored for the collision of e on H_2. The basic molecular structure looks like a somewhat distorted H_2 molecule to which is added a third, diffuse electron. We start from a different hypothesis. As the diffuse electron remains bound to the system, the basic structure is similar to that which the system has at large internuclear separations: an H^- ion and an H atom, both somewhat distorted by their mutual proximity. We are, therefore, seeking the autodetaching resonance states in a different region of Hilbert space.

Moreover, we demand that each of the orbitals, including that of the diffuse electron, shall be individually bound (i.e., have an orbital energy less than zero). More precisely, we demand that the expectation value of $p_r^2 + V(r)$ shall be less than zero. The rationale for such a restriction is that any electron which has a sum of radial kinetic energy plus potential energy greater than zero will directly escape in a time less than its orbital period. Such an electron has a radial speed which exceeds the escape velocity. Conversely, when this energy is less than zero, the diffuse electron is quasibound. It is unable to escape on its own; it will detach only if in an interaction with the core electrons it acquires sufficient additional energy at their expense. This is the hallmark of a Feshbach-type resonance.

The above definition does not exclude the possibility that the diffuse electron might also be trapped in part by a centrifugal barrier, $L^2/2mr^2$. Indeed, several previous studies have considered the diffuse electron to be p states trapped by the centrifugal barrier. However, in the present instance of a basis set consisting entirely of s states, the "radial energy" is the entire kinetic energy. The present approach allows the diffuse electron to be trapped even though it is entirely s wave in character. In this initial study, we limit ourselves to this possibility.

For the state under considerations, the orbital energy of the diffuse electron is less than zero if the energy of the "frozen two-electron core" of the H_2^- ion is greater than the energy of the full H_2^- ion. This "frozen core" is the H_2^- with the diffuse electron removed, while conserving the electronic wave function the core electrons had in the full H_2^- ion. The resonance condition is, therefore,

$$E(\text{ground-state } H_2) < E(H_2^-) < E(\text{frozen-core } H_2) . \tag{1}$$

The condition (1) permits autodetachment only if there is a rearrangement of the core, with a redistribution of energy between all three electrons. It is more general than the requirement that all three electrons shall be individually bound. It permits correlation (i.e., configurations mixing) between the core electrons, so long as the diffuse electron is described by a single-particle state. On physical grounds, the more tightly bound and therefore faster electrons can exhibit a correlated motion, which the slowly moving diffuse electron sees as generating a time-averaged potential. The diffuse electron moves too slowly to respond to any instantaneous details of core motion. However, a small amount of correlation between the diffuse electron and the core electrons is included in that the state is initially calculated with the diffuse electron on one of the two protons; a true $H^- + H$ state. At this stage of the calculation, the state has not yet been made an eigenfunction of the parity operator, and the singlet pair of the triad is the pair on the H^- center. It is at this point that the condition on the energy of the frozen core is introduced. Only afterward, in the calculation of the ${}^2\Sigma_u$ and ${}^2\Sigma_g$ energies is the appropriate parity rendered to the unsymmetric state by the operation of $1-\pi$ and $1+\pi$ on the unsymmetric state. The physical intuition guiding the construction of the state just described is that the H_2^- system consists of two distorted H atoms, with the diffuse electron traveling back and forth between the two centers, entering a temporary singlet state with the electron on the center it is on at the moment.

III. THE WAVE FUNCTION

The goal of the present study is the formulation of resonance states of the H_2^- system tailored for collisions of H^- on H. As a Feshbach-type formulation, it is accomplished by the construction of a Q subspace of Hilbert space which contains the resonance states as discrete levels. In the autodetaching region of internuclear separations ($R < 3a_0$), these levels should resemble the $H^- + H$ states which obtain for internuclear separations for which the $H^- + H$ states are true bound eigenstates of the complete electronic Hamiltonian. In the present case, Q subspace is the space constructed from the three lowest occupied orbitals of the $H^- + H$ system calculated at separation $R = 5.5a_0$, an internuclear separation at which the ion and atom are just beginning to significantly interact. The exponent of the diffuse Gaussian in the set of Gaussian functions is optimized, however, in order to verify that the resonance binding of the diffuse electron to the remainder of the system is not an artifact of the calculation.

The wave function of the H_2^- system is written in the form[44]

$$\psi = A\Phi_a(1)\Phi_b(2)\Phi_c(3)\chi , \tag{2}$$

where

$$\chi = (2)^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\alpha(3) . \tag{3}$$

Here A is the antisymmetrization operator, α and β denote spin-up and spin-down states. The single-particle states Φ_a and Φ_b are the two states on the H^-, while Φ_c is the single electronic state on the H. At this stage, ψ is not an eigenstate of the parity operator. That will come later. All three spatial states are constructed from the Q subspace described above. The two electrons on the H^- are taken to be in a singlet state, as is the case in H^- on H at large separations. The state given by Eqs. (2) and (3) can be alternatively written in the form

$$\psi = A(2)^{-1/2}[\Phi_a(1)\Phi_b(2) + \Phi_b(1)\Phi_a(2)]\Phi_c(3)\alpha(1)\beta(2)\alpha(3) . \tag{4}$$

Both forms yield the same result when the antisymmetrization, denoted by A, is carried out. At each internuclear separation, the states ψ are obtained by the generalized valence-bond (GVB) variational method.[45] In this approximation, the usual double occupancy of a molecular orbital is replaced by shared occupancy of a pair of orbitals. Hence, Φ_a and Φ_b in the square brackets of Eq. (4) describes the state of a singlet pair (the two electrons on the H^-), which constitutes a "closed shell." The unpaired Φ_c (the single electron on the H) is called an "open shell." The orbitals of the closed-shell singlet pair are not mutually orthogonal, but each is orthogonal to the open-shell state. As is usual in the GVB procedure, the state in the square bracket of Eq. (4) is rewritten in the completely equivalent form of a pair of natural orbitals,[46]

$$(2)^{-1/2}[\Phi_a(1)\Phi_b(2) + \Phi_b(1)\Phi_a(2)] = C_1\xi_1(1)\xi_1(2) + C_2\xi_2(1)\xi_2(2) , \tag{5}$$

where C_1 and C_2 are variational parameters. The molec-

TABLE I. Specification of the Gaussian functions and (unnormalized) basis functions. The basis function u_i is of the form $u_i=\sum_j A_j^i \exp[-\alpha_j^i(\mathbf{r}-\mathbf{r}_i)^2]$, where $\mathbf{r}_i$ give the location of the proton. The exponents and coefficients are listed in the last two columns. The Gaussians and basis functions used here are all s type. The exponent α_d of the diffuse function was variationally determined for each of the three ranges of internuclear separation. The variationally obtained values for α_d are also given.

Basis function	Component	Exponent	Coefficient
1	1	837.220000	0.0004490
1	2	123.524000	0.0035879
1	3	27.704200	0.0189896
1	4	7.825990	0.0782433
1	5	2.565040	0.2640259
1	6	0.938258	0.7135940
2	1	0.372145	1
3	1	0.155838	1
4	1	0.066180	1
5	1	α_d	1

$\alpha_d=0.013$ for $R>5.5a_0$
$=0.020$ for $3.0<R<5.5$
$=0.027$ for $R<3.0$

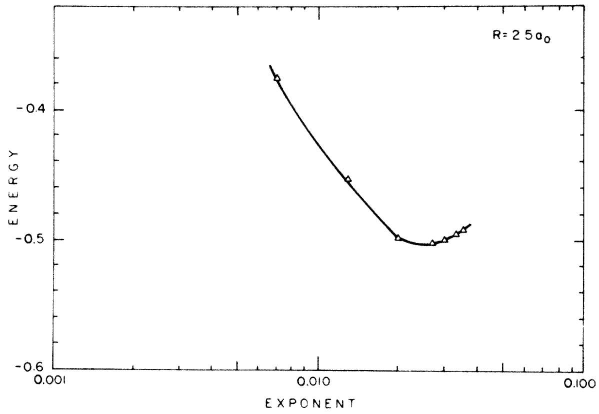

FIG. 3. Optimization of the exponent of the diffuse basis function at internuclear separation $R=2.5a_0$. The ordinate shows the binding energy in eV of the diffuse electron to the Q-space structure of the H_2 core. The abscissa gives the exponent in units of a_0^{-2}.

ular orbitals from which Q subspace was constructed are linear combinations of s type Gaussian functions in this first effort. Nine such s type Gaussian functions are needed for a good description of the hydrogen-atom wave function. The linear parameters were taken from Siegbahn and Liu,[47] who found this set to be comparable in flexibility to the four s type Slater functions which the second author used in a very precise calculation of the energy surface of a linear H_3 molecule. Six of the nine Gaussian functions centered on a given proton are contracted to form a single basis function. Each of the three remaining Gaussians is taken as a basis function in its own right. Finally, because it is common to negative ions that one of the electrons is very loosely bound, with a very diffuse wave function, a tenth, diffuse Gaussian s-type function was added to the above basis set as a fifth basis function. Thus, the basis set here employed consists of 10 basis functions, five about each center. They are listed in Table I. For internuclear separations greater than $5.5a_0$, this full basis set was used. For internuclear separations less than $5.5a_0$, the three lowest molecular orbitals calculated at $5.5a_0$ were used as Q space, but with two provisos. First, for internuclear separations $R<3a_0$, the 10 coefficients multiplying the Gaussian functions of the open shell (the H-atom wave function) were frozen at the values they had at $R=3$. And second, the values used for the exponent of the diffuse function were obtained from a preliminary optimization of the state with respect to variation of this exponent. The purpose of this optimization was not so much to improve the state as to demonstrate that this bound negative-ion orbital is not an artifact of the computation. In that optimization, the two orbitals for the H^- GVB pair were constructed only from Gaussian functions centered on that nucleus. These H^- orbitals were not permitted to have any component on the H center, a restriction which in retrospect we now think unnecessary. The optimization is illustrated in Fig. 3 and the values of the exponents listed in Table I. As shown in Table I, this optimization was carried out at one internu-

TABLE II. Molecular orbitals at sample internuclear distances. The last ten columns give the coefficients which multiply the ten basis functions described in Table I. These coefficients were obtained by the GVB variational procedure.

Orbital number	$R(a_0)$	Coefficients of the 10 basis functions									
		Basis functions on H center					Basis functions on H^- center				
	20	0.25	0.35	0.39	0.13	0.00	0	0	0	0	0
1	6	0.25	0.35	0.39	0.15	0.02	−0.01	−0.02	0	−0.07	−0.06
	2	0.30	0.43	0.46	0.22	0.04	−0.07	−0.08	−0.11	−0.17	−0.31
	20	0	0	0	0	0	0.27	0.39	0.35	0.11	0.02
2	6	0.01	0.02	0.02	0.02	0	0.27	0.39	0.35	0.11	0.02
	2	−0.07	−0.11	−0.11	−0.04	−0.01	0.30	0.43	0.38	0.14	0.08
	20	0	0	0	0	−0.02	−0.03	0	−0.02	−0.42	−0.66
3	6	0	0	0	0.09	0.13	−0.03	0	−0.02	−0.46	−0.75
	2	0.03	0.06	0.03	0.16	0.09	−0.04	−0.04	−0.13	−0.31	−0.88

TABLE III. Optimization of the exponent of the diffuse function. All energies are in atomic units. The energies shown below have been calculated with the H^- orbitals permitted to have components on both centers. Without the restriction that the H^- have no component on the H center, the *changes* in the energy E_0 from the values listed in Table IV are also shown below.

Value of exponent	Calculated energy $R=2.0a_0$	 $R=2.5a_0$	 $R=3.0a_0$
0.0001	-0.8685		
0.0005	-0.8709		
0.0010	-0.8725	-0.9426	
0.0030	-0.8755		
0.0050	-0.8762	-0.9480	
0.0080	-0.8757		
0.0100	-0.8748	-0.9491	-0.9821
0.0130		-0.9489	-0.9827
0.0150	-0.8721	-0.9487	
0.0180			-0.9829
0.0200	-0.8692	-0.9479	-0.9829
0.0230			-0.9828
0.0250	-0.8666		-0.9827
0.0270	-0.8656	-0.9468	
0.0300		-0.9464	

R	Change in energy
$2.0a_0$	0.0106 a.u. = 0.29 eV
$2.5a_0$	0.0023 a.u. = 0.01 eV
$3.0a_0$	0.0004 a.u. = 0.01 eV

clear separation in each of the three regions indicated, and the exponent obtained at that internuclear separation used for the entire region. For example, the exponent used for internuclear separations $R<3a_0$ was obtained by optimizing at $R=2.5a_0$. Table II gives the coefficients of the basis functions obtained by the GVB variational procedure for the molecular orbitals defined in Eq. (2).

As a test for sensitivity of the model to changes in detail, optimization of the exponent of the diffuse wave function was also carried out with the above restriction on the H^- wave functions relaxed. In this second attempt, the wave functions were permitted to have components on both centers, with the results shown in Table III. It can there be seen that this change in model causes the exponent to change significantly. At $R=2.5a_0$, the diffuse exponent changes from 0.027 (see Fig. 1) to 0.01 (see Table III). However, as Table III shows, the energies are quite insensitive to this change in the diffuse exponent. The change in energy, only 0.06 eV, is insignificant.

The wave function described above is not an eigenstate of the parity operator. Proper molecular states are constructed as

$$\begin{aligned}\psi_g&=N_+(\psi+\pi\psi)\,,\\ \psi_u&=N_-(\psi-\pi\psi)\,,\end{aligned}\tag{6}$$

where

$$\begin{aligned}N_+&=1/[2(1+S)]^{1/2}\,,\\ N_-&=1/[2(1-S)]^{1/2}\,,\end{aligned}\tag{7}$$

π is the parity operator and

$$S=\langle\psi\,|\,\pi\psi\rangle\ .\tag{8}$$

The labels g and u stand for the entire set of quantum numbers describing the states. Thus, the function ψ_g describes the parity symmetric state ${}^2\Sigma_g$, while ψ_u describes the antisymmetric state ${}^2\Sigma_u$. Defining E_0 as the energy of the original (unsymmetric) H^- + H state ψ, E_0 is given by

$$E_0=\langle\psi\,|\,H\,|\,\psi\rangle\ .\tag{9}$$

With M defined as the matrix element

$$M=\langle\psi\,|\,H\,|\,\pi\psi\rangle\ ,\tag{10}$$

then the energies associated with the actual molecular resonances ψ_g and ψ_u are given by

TABLE IV. Some variationally calculated quantities for the H^- + H system needed for the H_2^- resonances.

$R(a_0)$	S	M (a.u.)	E_0 (a.u.)	Resonance energy (frozen H_2 core) E (${}^1H_2$ core)	 E (${}^3H_2$ core)
20.0			-1.0136		
8.0	-0.1576	0.1655	-1.0126		
7.0	-0.1875	0.1980	-1.0119	-0.9935	-0.9979
6.5	-0.2066	0.2187	-1.0114		
6.0	-0.2298	0.2438	-1.0106	-0.9876	-0.9965
5.5	-0.2588	0.2752	-1.0096		
5.0	-0.3149	0.3348	-1.0077	-0.9689	-0.9920
4.5	-0.3766	0.3992	-1.0054	-0.9518	-0.9871
4.0	-0.4420	0.4664	-1.0019	-0.9258	-0.9783
3.5	-0.4990	0.5223	-0.9964	-0.8874	-0.9617
3.0	-0.4734	0.4977	-0.9825	-0.8903	-0.9490
2.7	-0.4385	0.4585	-0.9653	-0.8899	-0.9332
2.5	-0.4126	0.4271	-0.9468	-0.8832	-0.9172
2.25	-0.3811	0.3844	-0.9141	-0.8643	-0.8896
2.0	-0.3524	0.3367	-0.8656	-0.8283	-0.8492

$$E_g = E_0(1+M/E_0)/(1+S) \ , \tag{11a}$$

$$E_u = E_0(1-M/E_0)/(1-S) \ . \tag{11b}$$

The energy E_g lies above E_0, while the energy E_u lies below E_0. Table IV lists the value calculated for E_0, M, and S at various internuclear separations, from which the values for E_u in Fig. 1 and Eg is Fig. 2 were obtained.

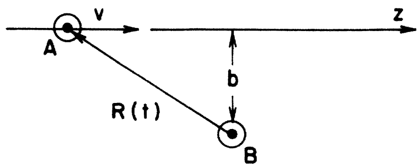

FIG. 4. Geometry of the straight-line trajectory.

IV. CHARGE EXCHANGE

The simplest charge-exchange process involving negative ions is the one which occurs in the collision under study,

$$H^- + H \rightarrow H + H^- \ . \tag{12}$$

The differential cross section for charge exchange is obtained by the same method used for H^+ on H. It involves the relative phase between the gerade and ungerade diatomic molecular states, which are degenerate at infinite internuclear separation (i.e., both before and after the collision interaction). In the case of H^- on H, ψ_g and ψ_u are the states of H_2^- which have been the subject of this study, given by Eqs. (6) and (7).

Denoting projectile and target by subscripts A and B, respectively, the projectile A is taken to be H^- before the collision interaction, with the H atom as the target B. With

$$\psi_A(R=\infty) = (2)^{-1/2}[\psi_g(R=\infty)+\psi_u(R=\infty)] \ , \tag{13a}$$

the initial state for the scattering process is given by

$$\psi(\mathbf{r},\mathbf{R}) = e^{ikZ}\psi_A \ . \tag{13b}$$

The final scattered state is given by

$$\psi_s = (2)^{-1/2}(|f_g|\psi_g e^{-i\gamma_g} + |f_u|\psi_u e^{-i\gamma_u})e^{ikR}/R \ . \tag{14}$$

Here, $|f_g|$ and $|f_u|$ denote the magnitudes of the respective scattering amplitudes, given by

$$|f_n| = (d\sigma_n/d\omega)^{1/2} = [(b/\sin\theta_n)/|d\theta_n/db|]^{1/2} \ , \tag{15}$$

where $\theta_n(b)$ is the classical deflection function for a trajectory calculated with potential energy $E_n(R)+1/R$. The subscript n stands for g or u, and E_g and E_u are defined by Eqs. (11a) and (11b), respectively. The phases are approximated by

$$\gamma_n(b) = \int_{-T_0}^{+T_0} E_n(t)dt = (1/v)\int_{-T_0}^{+T_0} E_n\sqrt{b^2+z^2}dZ \ , \tag{16}$$

where the integral is taken over the classical trajectory, $\mathbf{R}(t)$, here approximated by a straight line. In this straight-line approximation (see Fig. 4), used to calculate the γ's, γ_g and γ_u are functions of impact parameter, which must be reexpressed in terms of θ via the respective deflection functions $\theta_g(b)$ and $\theta_u(b)$. Expressing the g and u molecular states at time $+T_0$ in terms of H^- and H states, using the convention adopted in Eq. (13a),

$$\psi_s = \tfrac{1}{2}\psi_A(|f_g|e^{-i\gamma_g} + |f_u|e^{-i\gamma_u})e^{ikR}/R$$
$$+\tfrac{1}{2}\psi_B(|f_g|e^{-i\gamma_g} - |f_u|e^{-i\gamma_u})e^{ikR}/R \ . \tag{17}$$

The differential cross section for charge exchange is the square of the absolute value of the coefficient of ψ_B in the scattering amplitude given by Eq. (17). Thus

$$d\sigma_{\mathrm{ex}}/d\omega = \tfrac{1}{4}\,|\,|f_g|e^{-i\gamma_g} - |f_u|e^{-i\gamma_u}\,|^2 \ . \tag{18}$$

Factoring the unitary factor $\exp[-i(\gamma_g+\gamma_u)/2]$ from the quantity inside the vertical bars, the differential cross section can be rewritten in the form

$$d\sigma_{\mathrm{ex}}/d\omega = \tfrac{1}{4}[\,|f_g|^2 + |f_u|^2$$
$$-2|f_g|\,|f_u|\cos(\gamma_g-\gamma_u)] \ , \tag{19}$$

where

$$\gamma_g - \gamma_u = \int_{-T_0}^{+T_0}[E_g(t)-E_u(t)]dt \ . \tag{20}$$

At this point, the limits on the integral can be extended, letting T_0 go to infinity.

Equations (19) and (20) show that the differential cross section for charge exchange depends on the energy difference between the $^2\Sigma_g$ and $^2\Sigma_u$ states of H_2^-. This result is particularly important, because it suggests that experimental measurements of the differential cross section for charge exchange can experimentally determine this energy difference. As shown in Figs. 1 and 2, there is an enormous uncertainty in the energies of these two states. Moreover, experimental measurements on the differential cross section for charge exchange can also shed some light on the lifetimes of these two resonances. If the lifetimes are as long as 10^{-14} s, a clear oscillatory structure should be observed in the differential cross section for charge exchange. At the other extreme, if, as Demkov[38] suggests, there effectively are no resonance states, then no oscillatory structure will be observed. Unfortunately, there are as yet no differential cross-section measurements for this charge-exchange cross section; it is an extremely difficult experiment. Hopefully, the importance of these results to the theory of resonance states of H_2^- will encourage the undertaking of this experiment.

V. SUMMARY, RESULTS, AND CONCLUSION

In order to place the present work in proper context, this section will begin with a brief outline of the existing literature. There have been essentially two alternative approaches to collisions of e on H_2 and H^- on H, and in each of these two competing approaches, several different formalisms have been advanced. Feshbach projection operator theory[33] can be considered to provide the framework for one of the approaches. Because Feshbach projection operators are not unique, the several formalisms define (implicitly or explicitly) different projection operators and, consequently, somewhat different definitions of the resonance states. It is not surprising, therefore, that they produce different energy curves for the H_2^- autodetaching states. This is the approach of Taylor and collaborators,[34] the Siegert state method of Herzenberg and collaborators,[35] the O'Malley formalism,[48] the projection operator techniques of Chen,[49] and Bottcher,[50] and Domcke and collaborators.[51] There exist other examples of the Feshbach operator approach which are not included in this summary, because they have not been applied to the H_2^- system (see additional references contained in Refs. 34 and 51).

In the second general approach, the intermediate negative ion is not introduced explicitly. The collision reaction is interpreted as a direct transition between a bound $H^- + H$ state, and the continuum of $e + H_2$ induced by nonadiabatic couplings. Examples of this approach are the zero- and effective-range approximations,[38,39,52] the Fadeev equation treatment,[42] the *T*- and *R*-matrix formulations,[23] close-coupling calculations[23] and a recent work of Gauyacq,[52] which describes the dissociative attachment process by the principle of detailed balance from the associative detachment process, without invoking the formation of intermediate H_2^-. Finally, Berman *et al.*[53] claim to have found an unambiguous definition of the resonance states and their corresponding energy curves.

The present work fits into the category of a Feshbach projection operator formalism. It differs from previous works in that the basis set which defines Q subspace more resembles $H^- + H$ states than ordinary bound molecular states. The main difference is that the singlet pair shall be on one center, rather than the customary requirement that the singlet pair shall be the two electrons in the lowest energy state. For large separations, the two requirements are identical. It is only in the autodetaching region of internuclear separations that the two requirements become different.

A second departure from previous works is the refinement of the asymptotic condition on the Feshbach projection operators by the condition that the loosely bound electron in a negative ion shall indeed be bound. Not only must the radial parts of all wave functions in Q space vanish as r tends to infinity, but also the expectation value $\langle p_r{}^2 + V(r) \rangle$ must be negative, where $V(r)$ contains the full Hartree-Fock contributions of the $1/r_{ij}$ terms linking the loosely bound electron with the core. This has been accomplished by considering the energy of the frozen core. The method requires that the loosely bound electron shall be described by a single-particle state. Although the present work is limited to single-particle states for all three electrons, it was pointed out that the model allows configuration mixing in the core.

The energy curves of the ${}^2\Sigma_u^+$ and ${}^2\Sigma_g^+$ states of H_2^- here obtained are shown as the heavy solid lines in Figs. 1 and 2. Curve 10 for the ungerade ground state in Fig. 1 hardly shows that it has a minimum of 0.11 eV at $5.5a_0$. This is most likely an artifact. For smaller internuclear separations, its slope is similar to that obtained by Ostrovskii,[43] but displaced to higher energy. This curve crosses that of the neutral H_2 system at $3.95a_0$. The gerade excited-state energy curve is completely repulsive. It crosses that of the excited $b\,{}^3\Sigma_u^+$ state of neutral H_2 at $6.6a_0$. At internuclear separations below $3.5a_0$, it is very similar to that calculated by Bardsley and Cohen.[28] Wadhera and Bardsley[9] find that the energy curve associated with the ${}^2\Sigma_g^+$ state is very nearly parallel to that found for the $b\,{}^3\Sigma_u^+$ state of H_2, with an energy difference of the order of tenths of an meV between the two. This means that for all practical purposes, the emitted energy spectrum will be at zero energy. However, the experimental value of Esaulov[26] has a peak at 0.8 eV. Our energy curve and that of Bardsley and Cohen are in better agreement with the Esaulov results.

With the model described in the present work, together with the calculational limitations imposed by the GVB variational method, it has been possible to obtain resonance states only for $R > 2a_0$. For $R < 2a_0$, the diffuse electron remains unbound. It is possible that some lowering of this cutoff internuclear separation might be obtained by allowing configuration mixing in the core, but not much is to be expected. A critical internuclear separation for resonance states of the type $H^- + H$ appears to be a property of the model itself. When the two protons are close together, the diffuse electron almost equally overlaps both centers. The entire concept of the diffuse electron entering into a singlet spin state with the electron on the "nearer" H atom breaks down. Such a consequence is not necessarily a shortcoming of the model. It may very well be that there does exist a critical internuclear separation below which the diffuse electron is truly squeezed out, as Demkov[38] suggests. Resonances below that critical separation could, then, only be of the $e + H_2$ type, approaching the $e + He$ resonances.

Finally, it has been shown that the differential cross section for charge transfer in H^- on H collisions depends on the difference between the energy curves associated with the gerade and ungerade states. If this differential cross section can be experimentally measured, these measurements will greatly reduce the uncertainty in the energy curves seen in Figs. 1 and 2, and may perhaps shed some light on the possibility and location of a critical internuclear separation. Additionally, the measurements may also shed some light on the lifetimes of these as yet not well understood resonance states.

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