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Calculation of Resonances in the $\text{H}+\text{H}_2$ Reaction Using the Faddeev-AGS Method*

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Abstract

The $\text{H}+\text{H}_2$ reactive collision is described quantum mechanically in terms of valence-bond electronic states and the Faddeev-AGS equations for three-body collisions. The permutational symmetry of identical nuclei is considered within the present approach, which appears to avoid some of the difficulties associated with the use of electronically adiabatic states. A procedure based on the eigenvalue analysis of the K -matrix is used to locate resonances. Calculations probing the energy region of the lowest resonance in the H_3 system revealed one with an energy in good agreement with previous work.

Introduction

During the last few years, significant progress has taken place in the experimental and theoretical studies of reactive atom-diatom collisions. The experimental observation of dynamical resonances in the $\text{H}+\text{H}_2$ reaction by Nieh and Valentini [1] confirms the predictions of theoretical calculations concerning resonance energies [2], although there are still discrepancies in other aspects between the theory and experiment yet to be resolved. On the theoretical side, formal and computational developments [2-4] have made it feasible to treat three-atom systems heavier than H_3 , and to handle higher collision energies. However, all these developments are based on the single-surface adiabatic descriptions of chemical reactions.

An obscure aspect of the electronically adiabatic theories lies in the implementation of the nuclear permutational symmetry when the nuclei are identical. Traditionally, the (underlying) adiabatic electronic functions had been assumed to be totally symmetric under nuclear permutations. That this practice might not be appropriate for three identical atoms had been pointed out by Mead and Truhlar [5,6] in connection with the conical intersection of the ground and first excited potential energy surfaces of H_3 .

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Of course, the use of the electronically adiabatic description is due to its practical convenience rather than a theoretical necessity. It represents just one way of reducing the electrons plus nuclei problem into an effective nuclear dynamics problem. Other reduction procedures (not based on adiabatic electronic eigenstates) are clearly possible, and may even be computationally advantageous. Some time ago, [7] we presented a theory of three atom dynamics which does not use the adiabatic electronic representation. This theory, in effect, represents a combination of the valence-bond (VB) method (to handle the electronic structure) with the Faddeev theory [8] of three-particle dynamics (to describe the nuclear dynamics). In this approach, the construction of adiabatic potential surfaces is bypassed, and the nondiagonal matrix representation of the electronic Hamiltonian in the VB basis is directly used. As such, the questions of conical intersections with its attendant phase problems does not arise.

The implementation of nuclear exchange symmetry in our theory is transparent and extremely convenient, because the VB structures have, by construction, very simple transformation properties under the exchanges of identical nuclei. Furthermore, the dynamical theory encompasses all processes (i.e., nuclear as well as electronic rearrangements) allowed by the chosen VB basis. In this connection, our treatment is equivalent to a multisurface description with intersurface couplings included.

One advantage of the VB approach lies in the fact that the interaction potential for nuclear motion is not dominated by three-atom effects. (Strong three-atom forces present in adiabatic surfaces arises mostly from the electronic diagonalization.) This feature makes the treatment of the nuclear-rearrangement problem relatively easier compared to the one on an adiabatic potential surface. In fact, once the electronic degrees of freedom are eliminated by working in a VB space, the resulting effective equations for nuclear motion can be treated within the context of any theory of rearrangement scattering. In this work we use the Faddeev theory, which is advantageous whenever the total interaction is dominated by the sum of pair interactions. If the dimension of the VB space is denoted by N_e , the Faddeev treatment gives rise to $3N_e$ integrodifferential equations (or integral equations) in nuclear Jacobi coordinates (or momenta). In the case of three identical atoms, this number reduces to N_e by symmetry. Following a presentation of the scattering equations in the next section, and a discussion of permutational symmetry of nuclei in the third section, we present in the fourth section results for the resonances, or long-lived states, of H_3 .

Our calculations were done with a sum of pair potentials constructed from the lowest $^1\Sigma$ and $^3\Sigma$ potentials of H_2 . The parameters in these potentials were taken from work [9] where they are used to accurately interpolate numerical results for the H_3 ground potential energy surfaces [10]. Hence, the sums of pairs in our calculations, when diagonalized in the space of VB functions, yields the leading (London-type) term of the so-called LSTH potential. We compare our results with those of Hipes and Kuppermann [2b] and Cuccaro et al. [2d]. The agreement is quite good even though they used adiabatic potential surfaces, namely the PK2 surface [11] in Ref. [2b] and the LSTH surface [9] in Ref. [2d].

Faddeev Equations for H+H₂ Collisions

Let us label the three protons as 1, 2, and 3. The asymptotic partition $(i)(jk)$ will be referred to as the i th arrangement channel. The pair (jk) will also be labeled by the index i . The breakup channel $(1)(2)(3)$ will be given the index 0. The usual Jacobi coordinates of the i th arrangement are denoted by \vec{r}_i and \vec{R}_i , with the corresponding Jacobi momenta being \vec{p}_i and \vec{P}_i , respectively. Here, \vec{p}_i is the internal relative momentum of the pair (jk) , and \vec{P}_i the relative momentum of the i th proton with respect to the pair (jk) . In the center of mass frame, the kinetic energy operator H_0 of the nuclei has three equivalent representations: $H_0 = (p_i^2/2\mu) + (P_i^2/2M)$, $i = 1, 2, 3$, where $\mu = m_p/2$, and $M = 2m_p/3$ with m_p being the mass of the proton. Unless otherwise stated, we always use atomic units, and measure energy with respect to breakup into three H(1s) atoms. The eigenstates of H_0 will be written as $|\vec{p}\vec{P}\rangle_i (= |\vec{p}\rangle_i \times |\vec{P}\rangle_i)$, where the index i outside the ket indicates that the Jacobi momenta \vec{p}_i and \vec{P}_i of the i th arrangement have the values \vec{p} and \vec{P} , respectively.

The VB basis for total electronic spin $S = \frac{1}{2}$ is chosen as the two doublet covalent structures formed from the ground electronic states of three hydrogen atoms. In the spin-coupling scheme appropriate for arrangement $(i)(jk)$, these are denoted as $|s\rangle_i$, $s = 0, 1$, where s is the electronic spin of the diatomic (jk) . Denoting by $|\mathbf{s}\rangle_i$ the row of VB states $(|0\rangle_i, |1\rangle_i)$, the channel VB structures $|s\rangle_i$, $i = 1, 2, 3$, are related to each other by $|\mathbf{s}\rangle_i = |\mathbf{s}\rangle_j C_{ji}$, where C_{ji} are the 2×2 spin-recoupling matrices of three $\frac{1}{2}$ -spins for total spin $S = \frac{1}{2}$. The channel VB basis $|\mathbf{s}\rangle_i$ is non-orthogonal, with overlap matrix $\Delta_{ii} = {}_i\langle \mathbf{s} | \mathbf{s} \rangle_i$. The overlaps $\Delta_{jk} = {}_j\langle \mathbf{s} | \mathbf{s} \rangle_k$ represent recoupling of channel VB structures, and $\Delta_{jk} = C_{ji} \Delta_{ii} C_{ik}$ [7].

The transformation properties of the VB structures under nuclear permutations are easily determined as $P|s\rangle_i = (\pm 1)^s |s\rangle_{(Pi)}$ where P is a permutation operator belonging to S_3 , the $(+)$ sign applies when $P = P_{123}$ or P_{132} , and the $(-)$ sign when $P = P_{12}, P_{13}$, or P_{23} . The channel index (Pi) is the index of the arrangement that results when P is applied on the partition $(i)(jk)$. For example, $P_{23}|s\rangle_1 = (-1)^s |s\rangle_1$, $P_{12}|s\rangle_1 = (-1)^s |s\rangle_2$, and $P_{123}|s\rangle_1 = |s\rangle_2$. In fact, the basis $|\mathbf{s}\rangle_i$ transforms like the two-dimensional irreducible representation of the nuclear permutation group S_3 .

Denoting the projector onto the VB space with P^{VB} , the original Schrödinger equation will be replaced by $P^{\text{VB}}(E - H_0 - H_{\text{el}})P^{\text{VB}}|\Psi\rangle = 0$, where H_0 is the kinetic energy operator for the nuclei. The projector $P^{\text{VB}} = |\mathbf{s}\rangle_i \Delta^{-1} {}_i\langle \mathbf{s}|$, $i = 1, 2, 3$. The restriction of the electronic Hamiltonian H_{el} to the VB space is given by

$$V \equiv P^{\text{VB}} H_{\text{el}} P^{\text{VB}} = |\mathbf{s}\rangle_i \Delta_{ii}^{-1} {}_i\langle \mathbf{s} | H_{\text{el}} | \mathbf{s} \rangle_i \Delta_{ii}^{-1} {}_i\langle \mathbf{s}| \quad (1)$$

where we introduced the notation $V \equiv P^{\text{VB}} H_{\text{el}} P^{\text{VB}}$ since the VB representation of H_{el} will play the role of the (matrix) interaction for the nuclear motion. Defining the diatomic matrices V_j by the limits of ${}_j\langle \mathbf{s} | H_{\text{el}} | \mathbf{s} \rangle_j$ as $R_j \rightarrow \infty$, $j = 1, 2, 3$, we decompose ${}_1\langle \mathbf{s} | H_{\text{el}} | \mathbf{s} \rangle_1$ as a sum of these asymptotic limits and a three-atom term $V_{123}^{(1)}$, viz.,

$${}_1\langle \mathbf{s} | H_{\text{el}} | \mathbf{s} \rangle_1 = V_1 + C_{12} V_2 C_{21} + C_{13} V_3 C_{31} + V_{123}^{(1)} \quad (2)$$

In fact, Eq. (2) defines the three-atom interaction $V_{123}^{(1)}$ which vanishes as any

internuclear distance becomes large. We can now write the decomposition in operator form as

$$V = V_1 + V_2 + V_3 + V_{123} \quad (3)$$

with each diatomic interaction V_i being represented in its own channel VB basis by

$$V_i = |s\rangle_i \Delta_{ii}^{-1} V_i \Delta_{ii}^{-1} \langle s|, \quad i = 1, 2, 3 \quad (4)$$

The three-atom connected interaction V_{123} is representable in three equivalent ways as

$$V_{123} = |s\rangle_i \Delta_{ii}^{-1} V_{123}^{(i)} \Delta_{ii}^{-1} \langle s| \quad (5)$$

with $V_{123}^{(i)} = C_{i1} V_{123}^{(1)} C_{1i}$.

Note that the pairwise additive part of Eq. (2) is equivalent to the electronic Hamiltonian matrix of the "zero-overlap" diatomics-in-molecules (DIM) method [7]. As such, V_{123} is weak compared to $V_1 + V_2 + V_3$. In contrast, diagonalization of the pairwise additive part of Eq. (2) would yield potential surfaces strongly dominated by three-atom effects. Hence, by directly working in the nondiagonal VB representation, we avoid strong three-atom interaction matrices.

We expand the total wavefunction $|\Psi\rangle$ in the VB basis as $|\Psi\rangle = \sum_{s=0,1} |s\rangle_i |\psi_s\rangle_i$, where we can take $i = 1, 2, 3$. Collecting the nuclear functions $|\psi_0\rangle_i$ and $|\psi_1\rangle_i$ in the column $|\psi\rangle_i$, we have $|\psi\rangle_i = C_{ij} |\psi\rangle_j$. The effective equations for nuclear motion now become, for a total hamiltonian $H = H_0 + V$,

$$\Delta_{11}(E - H_0)|\psi\rangle_1 + F_{11}|\psi\rangle_1 + (V_1 + C_{12}V_2C_{21} + C_{13}V_3C_{31} + V_{123}^{(1)})|\psi\rangle_1 = 0 \quad (6)$$

where F_{ii} represents the momentum coupling terms arising from the action of H_0 on electronic functions $|s\rangle_i$. This equation represents two coupled partial differential equations for $|\psi_0\rangle_1$ and $|\psi_1\rangle_1$ in the six-dimensional nuclear-coordinate space.

In principle, any theory of rearrangement scattering can be used to solve the reaction dynamics embodied in Eq. (6). In this paper, we take advantage of the dominance of the pairwise additive portion of the interaction matrix, and reformulate Eq. (6) by an equivalent set of Faddeev equations. Instead of doing this in the most general form, we invoke the simplifying assumptions $\Delta_{11} = I$, $V_{123}^{(1)} = 0$, and $F_{11} = 0$, and construct the diatomic matrices, V_i , semiempirically using diatomic data. These approximations are tantamount to using the semiempirical zero-overlap DIM approximation. The matrices V_i are now diagonal, with diagonal elements being the singlet and triplet potentials of H_2 .

The Faddeev decomposition of the nuclear wavefunctions now reads [7,8]

$$|\psi\rangle_1 = |\psi_1^F\rangle + C_{12}|\psi_2^F\rangle + C_{13}|\psi_3^F\rangle, \quad (7)$$

with Faddeev components $|\psi_i^F\rangle$, $i = 1, 2, 3$, satisfying

$$(E - H_0 - V_i)|\psi_i^F\rangle = V_i \sum_{j=1}^3 (1 - \delta_{ij}) C_{ij} |\psi_j^F\rangle \quad (8)$$

Equation (8) represents six coupled integrodifferential equations for $|\psi_{is}^F\rangle$, $i = 1, 2, 3$, $s = 0, 1$. Since the V_i are diagonal, Eq. (8) in explicit form reads

$$(E - H_0 - V_{is})|\psi_{is}^F\rangle = \sum_{j=2,3} \sum_{s'=0,1} V_{is} C_{is,j s'} |\psi_{j s'}^F\rangle \quad (9)$$

where the $C_{is,j s'}$ are electronic-spin recoupling coefficients, and the V_{is} are the singlet ($s = 0$) and triplet ($s = 1$) potentials of the i th pair. One could study the rearrangement problem with Eq. (9) expressed in coordinate space. In particular, the wavefunctions $\psi_{is}^F(\vec{r}_i, \vec{R}_i)$ have the nice property of containing outgoing waves *only* in the $\vec{R}_i \rightarrow \infty$ limit.

In our implementation of the theory, we use the transition operator version of the Eq. (9). Denoting by $U_{j s', is}$ the multichannel operators (for transitions from the i th arrangement with the diatomic in the electronic state s to the j th arrangement with the diatomic in the state s'), they satisfy the Faddeev-AGS equations [7,8,12]

$$U_{j s', is} = (1 - \delta_{ji}) C_{j s', is} (E - H_0) + \sum_{k=2,3} \sum_{s''=0,1} C_{j s', k s''} t_{k s''}(E^+) G_0(E^+) U_{k s'', is} \quad (10)$$

where $G_0(E^+) = (E^+ - H_0)^{-1}$, and $t_{k s}(E^+)$ is the diatomic transition operator satisfying $t_{k s}(E^+) = V_{k s} + V_{k s}(E - H_0)^{-1} t_{k s}$. For a given initial channel (is), Eq. (10) represents six coupled equations (in six variables) for rearrangement operators. The operators $U_{j s', is}$ with $s' = 1$ or $s = 1$ do not have immediate physical meaning since triplet H_2 is not bound. However, they play an important role as pathways to $s = 0 \rightarrow s' = 0$ transitions, and would contribute to breakup amplitudes. If we denote by $U_{0 s_1, is}$ the operator describing transition from the (is) channel to a breakup channel with electronic spin s_1 for pair 1, then

$$U_{0 s_1, is} = \sum_{j=1}^3 \sum_{s'=0,1} C_{1 s_1, j s'} t_{j s'}(E^+) G_0(E^+) U_{j s', is} \quad (11)$$

Total breakup cross section will involve contribution from $U_{0 s_1, is}$ with both $s_1 = 0$ and $s_1 = 1$.

Let $|\phi_{sn}\rangle_i$ denote a set of basis functions for the i th pair. In particular, for the singlet case ($s = 0$) we take at least part of this basis to consist of the bound states of the singlet potentials. Here n collectively stands for collections of vibrational (v) and rotational (l, m_l) quantum numbers. The diatomic bound-state energies will be denoted by ϵ_{isn} . The product states $|\phi_{sn} \vec{P}\rangle_i$ will be referred to as channel states. All open channels as well as some pseudostates will be included in the set $\{|\phi_{sn}\rangle_i\}$ for $s = 0$. For $s = 1$, the basis set is somewhat arbitrary. Denoting the energy of an open channel state $|\phi_{sn} \vec{P}\rangle_i$ as $E_{isn P} = \epsilon_{isn} + (P^2/2M)$, the distinguishable-atom rearrangement amplitudes $T_{j s' n', isn}$ are given by the matrix elements

$${}_j \langle \phi_{s' n'} \vec{P}' | U_{j s', is}(E^+) | \phi_{sn} \vec{P} \rangle_i, \quad \text{with } E = E_{j s' n' P'} = E_{isn P}$$

Of course, below the breakup threshold only the elements with $s = s' = 0$ correspond to *on-shell* scattering.

To solve Eq. (10) in momentum space, we introduce partial-wave decompositions and vibrational-expansions, and obtain a larger set of one-variable integral equations.

Expansions in basis functions of angular variables are carried out in the standard manner [13]. The vibrational expansions are introduced in the form of separable expansions for the diatomic transition operators t_{is} . Using the Schwinger variational principle with the diatomic bases $\{|\phi_{sn}\rangle\}$ leads to [14]

$$t_{is}(E^+) = \sum_{nn'} \int d\vec{P} |\chi_{sn}\vec{P}\rangle_i \tau_{nn'}^{(is)}(e_P^+) {}_i\langle\chi_{sn'}\vec{P}| \quad (12)$$

where we defined the amplitudes

$$|\chi_{sn}\rangle_i = V_{is} |\phi_{sn}\rangle_i \quad (13)$$

In Eq. (12), $e_P = E - P^2/2M$, and the matrix $\tau^{(is)}$ is the inverse of the matrix $\{ {}_i\langle\phi_{sn}| V_{is} - V_{is} g_{0i}(e_P^+) V_{is} |\phi_{sn'}\rangle_i \}$. Here $g_{0i}(e^+)$ is the free Green operator for the i th pair. Note that in the present case the matrix $\tau^{(is)}$ is diagonal in angular momentum numbers, nondiagonal only in vibrational quantum numbers. At a given total energy E , the diatomic states $|\phi_{ns}\rangle_i$ satisfying $E > \epsilon_{ins}$ will give rise to poles in $\tau^{(is)}$ at $P = P_{ins} \equiv [2M(E - \epsilon_{ins})]^{1/2}$. Of course, these momenta P_{ins} are the physical on-shell momenta of the product states.

Defining the amplitudes

$$X_{js'n',isn}(\vec{P}', \vec{P}; E^+) = {}_j\langle\chi_{s'n'}\vec{P}'| G_0(E^+) U_{js',is}(E^+) G_0(E^+) |\chi_{sn}\vec{P}\rangle_i$$

and using the Eq. (12) in Eq. (11), we obtain a closed system of integral equations for these X amplitudes. Introducing the label $a \equiv (sn)$ with a notation signifying operator equations in the \vec{P} -space, these read

$$X_{ja',ia} = Z_{ja',ia} + \sum_{k=2,3} \sum_{a''a'''} Z_{ja',ka''} \tau_{a''a'''}^{(k)} X_{ka''',ia} \quad (14)$$

where the operators $Z_{ja',ia}$ have the P -space representation $Z_{ja',ia}(\vec{P}', \vec{P}) = {}_j\langle\chi_{s'n'}\vec{P}'| G_0(E^+) |\chi_{sn}\vec{P}\rangle_i C_{js',is}(1 - \delta_{ij})$. Equation (14) represents LS-type coupled integral equations in one vector variable. Note that rearrangement amplitudes $T_{js'n',isn}$ are given by on-shell matrix elements of the X amplitudes, viz., $T_{js'n',isn} = X_{js'n',isn}(P_{js'n'}, P_{isn}, E)$ with $E = \epsilon_{js'n'} + P_{js'n'}^2/2M = \epsilon_{isn} + P_{isn}^2/2M$.

To further reduce the number of variables, we introduce a partial-wave decomposition of the plane wave $|\vec{P}\rangle$, and work in the total angular momentum representation. For a given total angular momentum J , and with $b \equiv (sv/L)$, Eq. (14) becomes

$$X_{jb',ib}^J(P', P) = Z_{jb',ib}^J(P', P) + \sum_{k=2,3} \sum_{b''b'''} \int P''^2 dP'' Z_{jb',kb''}^J(P', P'') \times \tau_{b''b'''}^{(k)}(e_{P''}) X_{kb''',ib}^J(P'', P') \quad (15)$$

This equation can now be solved by a variety of methods such as quadrature discretization, Padé approximants, or Schwinger-type variational [13c].

Permutational Symmetry

To obtain the physical antisymmetrized amplitudes, we need to combine distinguishable-atom amplitudes $T_{js'n',isn}$ with appropriate coefficients. We use the prior-

antisymmetrization procedure by introducing the nuclear spin states into dynamical equations. Working with total nuclear spin $\Gamma = \frac{1}{2}$ or $\frac{3}{2}$, and denoting the nuclear spin-states by $|\gamma\Gamma\rangle_i$, with $\gamma(=0, 1)$ being the diatomic nuclear spin for pair i , we write the full channel states as $|c\Gamma\tilde{P}\rangle_i \equiv |s\rangle_i |\phi_{sn}\tilde{P}\rangle_i |\gamma\Gamma\rangle_i$. Taking $i = 1$ for our reference arrangement, $P_{23}|c\Gamma\tilde{P}\rangle_1 = (-1)^{s+\gamma+l+1}|c\Gamma\tilde{P}\rangle_1 = -|c\Gamma\tilde{P}\rangle_1$ for fermions. So we have the selection rule $s + \gamma + l = \text{even}$. Working always with channel states satisfying this rule, the antisymmetrized rearrangement amplitude is given by [12,15,16]

$$X_{c'c}^\Gamma = X_{s'\gamma'n',s\gamma n}^\Gamma = \delta_{\gamma'\gamma} X_{1s'n',1sn} + 2\langle\gamma'\Gamma|\gamma\Gamma\rangle_1 X_{2s'n',1sn} + 3\langle\gamma'\Gamma|\gamma\Gamma\rangle_1 X_{3s'n',1sn} \quad (16)$$

where $\langle\gamma'\Gamma|\gamma\Gamma\rangle_j$ are the nuclear-spin recoupling coefficients.

Defining $Z_{c'c}^\Gamma$ in a similar manner, the antisymmetrized amplitudes $X_{c'c}^\Gamma$ satisfy the analog of Eq. (14) with all arrangement indices dropped, and with channel labels changed accordingly. The identical particle version of Eq. (15) for a given J and Γ reads

$$X_{d'd}^{J\Gamma}(P', P) = Z_{d'd}^{J\Gamma}(P', P) + \sum_{d''d'''} \int P''^2 dP'' Z_{d'd''}^{J\Gamma}(P', P'') \tau_{d''d'''}(e_{P''}^+) X_{d''d}^{J\Gamma}(P'', P) \quad (17)$$

where we introduced the channel label $d \equiv (svlL\gamma)$. In effect, the prior symmetrization reduces the number of equations by a factor of 3. However, Eq. (17) has to be solved once for $\Gamma = \frac{1}{2}$, and once for $\Gamma = \frac{3}{2}$. The same kind of simplification can be achieved, without introducing the nuclear-spin structure, by block-diagonalizing Eq. (15) according to the irreducible representations of S_3 . Amplitudes labeled by irreducible representations would then be post-antisymmetrized by taking appropriate combinations with nuclear-spin states to generate $X_{d'd}^{J\Gamma}$.

The advantage of using a VB basis to eliminate electronic degrees of freedom becomes manifest in the implementation of nuclear permutation symmetry. The electronic-spin adapted VB structures (formed from electronically antisymmetrized products of atomic states) transform under nuclear permutations according to the irreducible representations of S_3 . Therefore, the nuclear wavefunctions can also be chosen to transform according to an appropriate irreducible representation of S_3 , with the net result being a simple and transparent implementation of nuclear permutational symmetry.

The situation is much more complicated in the adiabatic electronic description. According to the analysis of Mead [6], the distinguishable transition amplitudes $T_{in',ln}$ computed for H + H₂ collision at energies well below the conical intersection in a single-surface adiabatic theory (with diagonal nonadiabatic terms neglected), should be combined to yield the antisymmetrized amplitudes according to

$$T_{\gamma'n',\gamma n}^\Gamma = \delta_{\gamma'\gamma} T_{1n',1n} - 2\langle\gamma'\Gamma|\gamma\Gamma\rangle_1 T_{2n',1n} - 3\langle\gamma'\Gamma|\gamma\Gamma\rangle_1 T_{3n',1n} \quad (18)$$

Note the $(-)$ signs in comparison to Eq. (16). This additional sign change in distinguishable exchange amplitudes comes about from the presence of a conical

intersection and its attendant complications concerning the phase of the adiabatic electronic function.

These complications do not arise in the formalism based on a nondiagonal VB description. Since the permutation properties of VB structures are properly taken into account, the usual post-symmetrization rules continue to hold, but with indistinguishable-atom amplitudes computed within the framework of Eqs. (6) or (9) or their integral-equation versions. In this connection, we remark that the selection rule ($s + \gamma + l = \text{even}$) is valid not only in the separated atom-diatom asymptotic regions, but all over the nuclear configuration space. This observation sheds some light on the question of nuclear-permutation symmetry in single-adiabatic-surface theories. Let us consider the lowest potential surface and the corresponding adiabatic electronic function that would result from diagonalizing our VB-electronic Hamiltonian matrix. This adiabatic function would be a combination of the VB structures $|0\rangle_1$ and $|1\rangle_1$ with nuclear-geometry-dependent coefficients. In studying the nuclear dynamics on this lowest potential surface there is no way to enforce the above selection rule, except for the separated atom-diatom regions. Imposing the asymptotic selection rule for singlet H_2 (i.e., $l + \gamma = \text{even}$) over the whole nuclear space would clearly be inconsistent.

Calculation of H_3 Resonances

In the computational implementation of the theory outlined in the previous two sections, we use the K -matrix version of the Eq. (17) which is obtained by replacing the integral over P'' with a principal-value prescription. The present work considers only the $J = 0$ and $\Gamma = \frac{1}{2}$ state of the H_3 system. In this case the channel index d stands for $(svl\gamma)$ since $L = l$. If we use N_V vibrational and N_R rotational levels of H_2 , Eq. (17) represents a set of $2N_V N_R$ integral equations for $J = 0$, $\Gamma = \frac{1}{2}$. To effect the discretization of these equations, a cut-off value P_{\max} in the P -variable is introduced and the interval $[0, P_{\max}]$ is divided into subintervals with a low order Gauss-Legendre quadrature being applied in each subinterval. Denoting with N_Q the total number of quadrature points, the resulting matrix problem is of dimension $2N_V N_R N_Q$. In the present work typical values for P_{\max} and N_Q are 20 and 60 au, respectively.

In the present set of calculations we have probed the energy region of the lowest resonance reported by Kuppermann and co-workers. Vibrational and rotational bases contained $v = 0-5$, $l = 0-5$. Convergence of, e.g., transition probabilities are not guaranteed with these bases. However, spectral features such as resonance energies can be expected to be less susceptible to basis-set truncations. This expectation is in fact born out in Table I, which shows the resonance energies obtained with different N_V and N_R values. With the largest basis (namely $N_V = 6$ and $N_R = 6$) we find $E_R = -0.1504$ au with respect to breakup, or 0.655 eV with respect to the bottom of the potential well in the asymptotic $H + H_2$ channel. The value reported by Kuppermann group is 0.61 eV for the PK2 surface and 0.65 eV for the LSTH surface.

A more limited set of calculations (with $N_V = 5$, $N_R = 4$) have been performed to locate the second lowest resonance whose energy is reported [2d] at 0.847 eV

TABLE I. Convergence study for the resonance energy E_R around the energy -0.15046 au with respect to 3H(1s). Here N_V and N_R are the number of diatomic vibrational and rotational basis functions, respectively.

N_V	N_R	E_R (au)
5	5	-0.15012
5	6	-0.14974
6	5	-0.15060
6	6	-0.15046

for PK2 surface and 0.880 eV for the LSTH surface. We found this resonance at $E_R = -0.1426$ au with respect to breakup or 0.867 eV above the bottom of asymptotic H₂ well.

To locate the resonances we search for the poles of the K -matrix which in the vicinity of an isolated resonance pole assumes the Breit-Wigner form

$$K_{d'd}^{(BW)} = \frac{1}{2\pi} \frac{\gamma_d \gamma_d}{E - E_R} \quad (19)$$

where E_R is the resonance energy and γ_d is the decay amplitude into the channel d . Total width

$$\Gamma = \sum_d (\gamma_d)^2 \quad (20)$$

with $(\gamma_d)^2$ being the partial width for the channel d . The pole behavior can usually be uncovered with an energy resolution of 0.00025 au. However, instead of monitoring the full K -matrix it is much more convenient to follow the eigenvalues of the K -matrix. Diagonalization of the K -matrix yields N_{open} eigenvalues κ_i and corresponding eigenvectors \mathbf{z}_i

$$\mathbf{K} \mathbf{z}_i = \kappa_i \mathbf{z}_i \quad (21)$$

When E is close to resonance, one of the eigenvalues of K exhibits a pole behavior. Denoting the resonant eigenvalue by κ_R , its energy dependence near the resonance can easily be found from Eq. (19) as

$$\kappa_R = \Gamma / [2\pi(E - E_R)] \quad (22)$$

Table II shows the energy dependence of the resonance eigenvalue of the K -matrix. The corresponding eigenvector, which is practically energy independent in the vicinity of the resonance, is shown in Table III. Branching fractions namely $(\gamma_d)^2 / \Gamma$, are directly obtained by squaring the components of the (normalized) resonant eigenvector. Table III indicates that the branching ratios are not yet stabilized with respect to vibrational basis size. It nevertheless suggests that the largest contribution to the lowest resonance state comes from the $v = 0$, $l = 2$ states of H₂.

TABLE II. K -matrix eigenvalues κ_i ($\kappa_i = \kappa_R$) for $J = 0$, $S = 1/2$ and $\Gamma = 1/2$ around the first resonance. The basis set included $N_V = 6$ and $N_R = 6$ functions.

E_R (au)	κ_1	κ_2	κ_3	κ_4	κ_5	κ_6
-0.15050	-7.00	-0.75	-0.36	0.11	0.33	0.61
-0.15045	32.814	-0.77	-0.4	0.09	0.31	0.53
-0.15040	4.217	-0.78	-0.43	0.06	0.28	0.48

The truncations of the vibrational and rotational bases in the present work were made solely to reduce the computational requirements. For the largest basis employed an algebraic equation system of dimension 4320 has been solved. Calculations designed to achieve full convergence with respect to both vibrational and rotational expansions, and search for higher energy resonances will be continued in future work.

In passing we note that the eigen-analysis of the K -matrix provides a very practical tool to uncover resonances. Nonresonance eigenvalues change rather smoothly with energy. Consequently, resonance eigenvalues can be identified on an energy grid of 0.0005 au (about 0.014 eV). Once a resonance behavior is detected it can be further bracketed with a few more runs such that the absolute value of the resonance eigenvalue is in the order of 100 or higher. At this point the Breit-Wigner form (without the background term) can safely be used since background terms are entirely dominated by the resonance pole. In fact, the eigenvalue analysis of the K -matrix also provides a convenient tool to separate the resonance and background contributions.

It is also worth noting that the time-delay matrix analysis becomes extremely simple once the resonance is bracketed to a precision sufficient for $K^{(BW)}$ to be dominant. In particular the need to numerically differentiate the S -matrix is alleviated. If the $K^{(BW)}$ is valid then the resonance eigenvalue of the time-delay matrix is simply given as

$$\tau_R = \Gamma / [(E - E_R)^2 + \Gamma^2/4] \quad (23)$$

Conclusions

The present calculations and those of Kuppermann and co-workers differ in two important respects: Firstly, our treatment is based on a nondiagonal 2×2 interactions matrix whereas Refs. [2b] and [2d] use adiabatic potential energy surfaces.

TABLE III. Branching fractions P_{ij} for decay from the resonance with energy $E_R = -0.15046$ au

N_V	N_R	P_{00}	P_{01}	P_{02}	P_{03}	P_{04}	P_{05}
5	6	0.018	0.331	0.389	0.110	0.113	0.040
6	6	0.038	0.015	0.521	0.233	0.181	0.010

Upon diagonalization our 2×2 matrix interaction would reproduce the leading London term of the LSTH surface. However, our treatment inherently includes the (approximate) upper surface as well as the electronic coupling between the two surfaces. Secondly, the treatments of the nuclear dynamics are different. We use momentum space integral equations, whereas Kuppermann and co-workers solve the nuclear Schrodinger equations in coordinate space using hyperspherical coordinates. Although our calculations are not fully converged, the broad agreement with respect to the positions of the two lowest resonances in the two approaches is encouraging.

Our approach has no problems associated with conical intersections and nuclear exchange symmetry, which seem to plague the electronically adiabatic theories [5,6,17]. The conical-intersection problem will certainly be more difficult to handle at larger collision energies (about 3 eV) probing the intersection region. In fact, at such energies a two-surface treatment (with non-adiabatic couplings included) will certainly be needed. In such a case a diabatic approach of the type discussed in this paper might be more appropriate.

Note that our equations are still valid even above the breakup threshold, perhaps up to 1–2 eV above the threshold for $H(1s) + H(1s) + H(1s)$. In order to cover even higher energies a more extended VB basis would be needed. In principle, we could take the 20-structure DIM model of Roach and Kuntz [18], and use it in our Faddeev theory. In this case, we would have 20 coupled integral equations in six variables, compared to the two equations in the present study. Of course, the other problem in using Eq. (17) at high energies is the enormous number of vibrational-rotational states that would have to be included. At energies well above the breakup, a perturbative approach based on Eq. (17) might be more suitable.

The practical bottleneck in the present computational implementation of our theory is in the quadrature discretization step. Typically, 50–60 quadrature points are needed, making the final matrix dimension (for $J = 0$) $N_e N_V N_R N_Q$ with N_e being the number of VB structures, N_V the number of vibrational states, N_R that of rotational states, and N_Q the number of quadrature points. We hope to reduce this dimension by replacing the quadrature-discretization method with a Schwinger-type variational method. Should 15–20 basis functions in relative momentum be sufficient, we could easily achieve convergence with respect to N_V and N_R . Insight from coordinate-space calculations [19] indicates that $N_V = 5$ –6 and $N_R = 8$ –12 might be adequate to achieve convergence. Taking for the sake of argument $N_V = 5$, $N_R = 10$, and $N_Q = 15$, our theory would lead to a matrix problem of dimension $750 N_e$. The present case of $N_e = 2$ would be easily accommodated with present day computational power, and even the use of more extended VB bases (such as the 20-structure DIM model [18]) would not be out of sight. In particular, the treatments of reactions like $D + H_2$, $H + H_2^+$ and other systems describable with small VB bases would be feasible. According to our general theory, the matrix sizes will approximately be $4 N_V N_R N_Q$ for $D + H_2$, and $3 N_V N_R N_Q$ for $H^+ + H_2$ [7].

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