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Diabatic states via a diabatic Hamiltonian

Arnold Russek and Richard J. Furlan
Department of Physics, The University of Connecticut, Storrs, Connecticut 06269

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A new class of diabatic states for atom-atom and atom-molecule collisions is obtained by formulating a diabatic Hamiltonian. The true Hamiltonian describing the collision system is decomposed by means of topologically defined projection operators into a diabatic Hamiltonian plus an interaction term. A pseudosymmetry operator, which commutes with the diabatic Hamiltonian, is constructed from these same projection operators. The diabatic states are simultaneous eigenstates of the diabatic Hamiltonian and the pseudosymmetry operator. They cross and maintain their character through the crossing region. Such level crossings do not constitute a violation of the noncrossing rule, because the diabatic states involved have different pseudosymmetry. The diabatic states are coupled by the interaction term of the Hamiltonian. A set of coupled equations of motion for the amplitudes of the diabatic states is derived from the time-dependent Schrödinger equation. The $(\mathrm{HeH}_2)^+$ triatomic molecular ion is considered as an example. A pseudoreflection operator is constructed from the projection operators, which reduces to the usual reflection operator in those geometries for which the potential energy has true reflection symmetry. Pseudoinversion symmetry is also considered for this molecular system, treating the H_2 at small separations as a near He. In addition, a new configuration constant of the motion is constructed for multielectron systems which is not an extension of a conventional symmetry. The diabatic states obtained in this work predict a recently observed excitation of He to an $n=2$ state in $\mathrm{H}_2{}^+$ on He collisions.

I. INTRODUCTION

For the quasimolecular states used in the theoretical analyses of atomic and molecular collision processes, it is generally accepted that "states of the same symmetry do not cross." This is the so-called "noncrossing rule" of von Neumann and Wigner,[1] a good presentation of which can be found in Landau and Lifshitz.[2] Figure 1 shows the molecular geometry of the $(\mathrm{HeH}_2)^+$ molecular system, which is used as an illustrative example in this work. Figures 2(a) and 2(c) show molecular energy diagrams for this system (actually, a cut through the energy surface) for $r=2$ and $\gamma=90°$. Figure 2(a) shows the *ab initio* adiabatic energies only, while 2(c) shows the diabats as well. For $\gamma=90°$, the molecular geometry has isosceles triangle symmetry, designated by C_{2v}. In this case, the electronic Hamiltonian has two reflection symmetries, so that the respective reflection operators are constants of the motion. As a result, the electronic states are simultaneous eigenstates of the Hamiltonian and of both reflection operators. The adiabatic energy curves of Fig. 2(a) show eigenstates of the Hamiltonian belonging to different eigenstates of one of the symmetry reflection operators and which do cross. These states are identified in Fig. 2(c). One is even, the other odd under reflection in the y-z plane. The third state of Fig. 2(a) cannot be discussed in terms of reflection symmetry only, and will be taken up later.

For molecular geometries off C_{2v} symmetry, there is but a single symmetry constant of the motion, reflection in the x-y plane containing the nuclei. This is termed C_s symmetry. Since all of the orbitals encountered in this work have positive reflection symmetry in this plane (Σ states), this constant of the motion will be suppressed in the notation. For the C_s case, the adiabatic energy curves, seen as the dashed curves of Fig. 2(b), do not cross, in accordance with the noncrossing rule. In the vicinity of such an avoided crossing, adiabatic states of the same symmetry rapidly change character to make the adiabatic energy levels avoid each other. Because they are rapidly changing in a narrow range of internuclear separations (passed through in a short time interval even in modest energy collisions), the electronic motion is unable to respond quickly enough to follow adiabatic behavior. Rather, the time-dependent electronic state main-

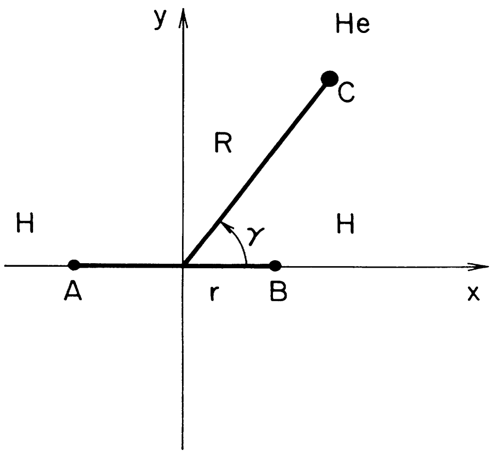

FIG. 1. The molecular geometry.

tains its character, and jumps over the avoided crossing. This behavior is termed *diabatic*,[3] following either the solid or the dot-dot-dashed curves of Fig. 2(d).

Smith[4] has defined diabatic states as those for which $\nabla_R \psi = 0$ in the crossing region; states which do not change at all will certainly maintain their character through this region. Such a definition works well in those instances in which the crossing region is narrow and the diabatic states themselves are slowly changing with R. There are, however, cases for which these implied conditions are not met, and the Smith definition of diabatic states presents problems. It was pointed out by Delos and Thorson[5] that the diabatic states thus generated do not even follow the nuclear motion. Such behavior can be tolerated if the crossing region is narrow, but not if it is broad. Delos and Thorson and Delos[6] suggest using electron translation factors to remove this particular failing of the Smith definition.

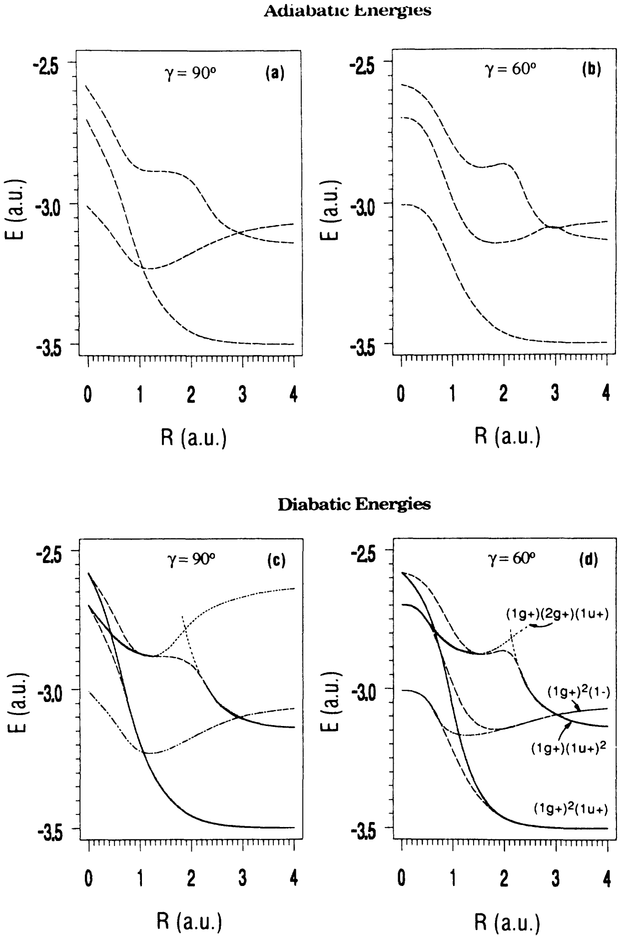

FIG. 2. Molecular energy levels for the case $r=2$, appropriate for collisions of H_2^+ on He. (a) and (b) show the adiabatic energies for the three lowest states as functions of R, for $\gamma = 90°$ and 60°, respectively. (c) and (d) show these same energies, but include the diabatics as well. The pseudosymmetry designations are given in (d). In all cases, the adiabatics are shown as dashed curves. The solid curves show states of $+1$ symmetry ($\gamma = 90°$) or pseudosymmetry ($\gamma = 60°$). The dot-dot-dashed curves show states of -1 symmetry or pseudosymmetry. The dotted curves indicate interpolations, where only fragmentary *ab initio* values (in the crossing region and at $R = \infty$) are available.

In this work, an alternate strategy is adopted following O'Malley,[7,8] who defined a diabatic Hamiltonian by means of projection operators. The formulation of the diabatic Hamiltonian, together with the projection operator constants of the motion, is presented in Sec. II. Section II also includes the derivation of the equations of motion for the amplitudes of the diabatic electronic states. In several respects, the present formulation is similar to that of Kubach *et al.*,[9] who followed the O'Malley approach. However, there are important differences between the present formulation and that of Kubach *et al.* which will be discussed in Sec. III. Section III is devoted to a discussion of the projection operators themselves. The projection operators used in the present work are *topologically*[10] defined projection operators, which will be motivated in this section and more fully described in Sec. III.

In a collision problem, a different basis set is used for each internuclear separation; thus a different projection operator is defined for each internuclear separation. To speak of a projection operator in a collision problem, it is necessary to define in some compact way the basis set for each internuclear separation. When the collision geometry is such that point symmetries (such as even-odd or gerade-ungerade) hold, these topological invariants of the motion determine the "character" of the state. The names simply describe the eigenvalues of commuting operator constants of the motion reflection and parity. When the collision system is not characterized by one of the point symmetry groups, it is still possible to find topological invariants of the motion during the collision process for the diabatic Hamiltonian, in terms of the nodal structures of the electronic states.[10-12] The topological projection operators which select out the desired nodal structures are constructed from prescribed linear combinations of Gaussian primitive elements with the same (or nearly the same) exponents, but on different centers. The construction is best described in terms of an example. The basis set used in this work consisted of four s-type and two p-type atomic functions, similar to the set used by Brown and Hayes[13] for $(\mathrm{HeH_2})^+$. That set was adapted from Edmiston *et al.*,[14] which in turn was adapted from Huzinaga.[15] It consists of five s-type Gaussians on each H contracted to four s-type "atomic orbitals," and six s-type Gaussian functions on the He contracted to four s-type "atomic orbitals." The exponents of the p-type Gaussians are here taken to match those of the second and third most diffuse s-type Gaussians. In the optimized set of primitive elements used by Brown and Hayes,[13] the third Gaussians centered on H_A and H_B each have exponent 0.33, while the corresponding third Gaussian on the He center at C has exponent 0.43. With these, the third element in the basis sets defining the pseudosymmetries at $r=2.0$, $R=3.0$ and $\gamma=60°$ are

$$\phi_{3g+} = e^{-0.33 r_A^2} + e^{-0.33 r_B^2} + 6.37 e^{-0.43 r_C^2} ,$$

$$\phi_{3u+}=e^{-0.33r_A^2}+e^{-0.33r_B^2}-0.74e^{-0.43r_C^2}\,,$$

$$\phi_{3-}=e^{-0.33r_A^2}-e^{-0.33r_B^2}\,.$$

The first gives the $i=3$ element of the basis set ϕ_{ig+} spanning the space of $g+$ pseudosymmetry. The others give the $i=3$ basis elements of the $u+$ pseudosymmetry and $-$ pseudosymmetry. The pseudosymmetry nomenclature (described in Secs. III C and III D) is not important at this point. What is important is how corresponding primitive elements on the respective centers are grouped together to construct a basis set used to define the topological projection operators. The situation is somewhat more complicated than simply using the ϕ_{ig+}, ϕ_{iu+}, and ϕ_{i-} to construct the topological projection operators. The three-spaces must be made orthogonal to one another, a procedure given in Sec. III. The final basis elements of the complementary subspaces will be denoted by u_{ig+}, u_{iu+}, and u_{i-}.

The u's, when thus obtained, define the pseudosymmetries at vanishingly small collision velocities. At finite collision velocities, each of the Gaussians that make up the ϕ_i can be multiplied by the electron translation factor appropriate to the center it is on. This will yield moving diabatic states that satisfy the proper boundary conditions.[5] However, this step is not required for self-consistency of the present formulation. By contrast, electron translation factors were shown by Delos and Thorson to be essential in their approach. The incorporation of electron translation factors into the present formulation will necessitate revamping the integrals package of existing quantum-chemistry programs, a task which is extremely difficult, but not impossible. The subject of moving diabatic states in the present formulation will be dealt with in a future publication.

It must be clear that the *ab initio* calculations of the present work obtain only *adiabatic* states. The contractions of Gaussians on different centers, inherent in the basis sets defining the topological projection operators, are not incorporated in present-day quantum-chemistry codes. Moreover, adiabatic states are even desirable in an exploratory study such as the present work. They demonstrate that away from the interaction region, the adiabatic states do have the pseudosymmetries of the crossing diabats, and that in the interaction region, the adiabatic states are linear combinations of these crossing diabats.

The use of combinations of Gaussian primitive elements permits the specification of nodal structure, while at the same time allowing the flexibility needed to optimize electron orbitals. It is this flexibility to optimize orbitals that gives the present formulation an advantage over the previous ones: concisely stated, it is the superiority of multiconfiguration calculations over simple configuration-interaction calculations. The projection operators are thus intimately tied in with quantum-chemistry programs. Because the Gaussian primitive elements form a nonorthogonal basis set, the topological projection operators must be defined in terms of a nonorthogonal basis set. The necessary mathematical development is presented in Sec. III B. The Gaussian primitive elements here used were taken from the existing literature, which did not take pseudosymmetry into account. To the extent that the pseudosymmetry concepts here presented are accepted, future Gaussian primitive sets should be constructed with corresponding primitive sets having equal exponents.

Historically, the use of nodal structure to characterize the states of a quasimolecule was first introduced by Morse and Stueckelberg[11] for diatomic quasimolecules. They characterized the (diabatic) states of a diatomic quasimolecule in terms of the number of nodes in the angular part of the single-particle wave function separated in prolate spheroidal coordinates. The characterization of diabatic states via nodal structure in the diatomic quasimolecule was made more explicit by Barat and Lichten,[12] who defined diabatic states in terms of the number of nodes on a line joining the two centers. The use of nodal structures to characterize diabatic states was generalized by Russek and Furlan[10] to the multicenter case by focusing on the topological properties of the nodal structure of the single-particle orbitals. In Sec. IV of the present work, it will be established that the number of nodal surfaces does not necessarily remain invariant as the nuclear geometry varies; but only the odd or even quality of the number of intersections with a line (or curve) joining the centers. This topological concept of the nodal structure is more general than the point symmetries, and includes them as special cases. Hence the projection operator constants of the motion are termed "pseudosymmetry" operators.

The true point symmetry operators commute with the full Hamiltonian, and states of different true symmetry are therefore not coupled by the equations of motion. For example, in a collision of He^+ on He, parity is a constant of the motion. If the initial electronic state is gerade, it will stay gerade throughout the entire collision process. From the standpoint of electronic excitation, this case is uninteresting. The levels are well characterized and cross, but no electronic excitation occurs. On the other hand, the pseudosymmetry constants of the motion commute only with the diabatic Hamiltonian, not the full Hamiltonian. Therefore the equations of motion for the coefficients of the diabatic states will couple states of different pseudosymmetry. These equations, derived in Sec. II, are rigorous and exact.

In collisions of He^+ on H_2, or H_2^+ on He, the two protons constitute a system that is similar to a He nucleus, an idea advanced by Dowek *et al.*[16] As a result, the collision system has pseudoparity symmetry, which is built into the diabatic Hamiltonian in Sec. III. The diabatic states obtained in this work predict that a Rydberg state of He is excited in low-energy collisions of H_2^+ on He [see Fig. 2(d)], contrary to current models. The diabatic crossing involved is between orbitals of a'_{u+} and a'_- pseudosymmetry. The projection operators used by Kubach *et al.*[9] were defined in terms of the $1a'$ and $2a'$ *adiabatic* orbitals, which are linear combinations of the topologically determined diabatic orbitals. Kubach *et al.*[9] could not, therefore, obtain this diabatic crossing, and appear not to have suspected it. Nor was this diabatic crossing suggested in the earlier work of Hopper.[17] Both found the two-electron diabatic crossing between the $\mathrm{He}^+ + \mathrm{H}_2$ and the $\mathrm{He} + \mathrm{H}_2^{+*}$ repulsive state. The Rydberg excitation of He predicted in the present work has in fact been observed by Quintana *et al.*[18]

II. THE DIABATIC HAMILTONIAN

O'Malley[7,8] has suggested that diabatic states can be defined in terms of a diabatic Hamiltonian, here denoted by H_D,

$$H_D = QHQ + PHP \ , \tag{1}$$

where

$$P^2 = P, \quad Q^2 = Q, \quad PQ = 0 \ . \tag{2}$$

If P and Q together span all of Hilbert space, then $P + Q = 1$. However, the goal of this work is a formulation which can be incorporated into quantum-chemistry *ab initio* computer programs, which employ a finite (Gaussian) basis set. Since this last condition is not fulfilled in the intended application, it will not be used in the formulation. Thus H denotes not the true Hamiltonian of the collision system, but the projection of that Hamiltonian onto the basis set $P + Q$:

$$H = (P+Q)H_{\text{true}}(P+Q) \ . \tag{3a}$$

Realistically, H, as defined by (3a) is what is actually used in a collision calculation. It can be written as the sum of the diabatic Hamiltonian plus an interaction term,

$$H = H_D + H' \ , \tag{3b}$$

where

$$H' = PHQ + QHP \ . \tag{4}$$

In a sense, the diabatic states provide the zeroth-order description of the collision process. However, the formulation here presented will be rigorous and complete; H' need not be small. Using the properties of the projection operators listed in Eq. (2), it is not hard to show that both P and Q commute with H_D:

$$\begin{aligned} P(QHQ+PHP) &= PQHQ + PPHP = 0 + PHP = 0 + PHPP \\ &= (QHQ + PHP)P \ . \end{aligned}$$

This proves that

$$PH_D = H_D P \ . \tag{5a}$$

Exactly the same type of proof yields the result

$$QH_D = H_D Q \ . \tag{5b}$$

Thus, P and Q are constants of the motion for H_D, but not for H itself. The pseudosymmetry operator π is defined to be

$$\pi = P - Q \ , \tag{6}$$

which by (5a) and (5b) also commutes with H_D. The eigenvalues of π are $+1$ and -1, belonging to eigenfunctions of H_D in P space or Q space, respectively. This makes π a generalization of this reflection or parity operator, either of which it includes as a special case. This latter can be accomplished by making P and Q the operators which project onto even and odd functions. It is a generalization in the sense that π can be defined via Eq. (6) even when exact reflection or inversion symmetry does not hold.

Because H_D and π commute, they have simultaneous eigenstates. The diabatic states are defined to be these simultaneous eigenstates. Eigenstates of H_D which belong to different eigenvalues of π are not inhibited from crossing.[1,2] It should be noted that all this can be done without explicitly defining P and Q. The formulation only provides a framework for discussing diabatic states; the quality of the diabatic states obtained depends on how well P and Q correspond to the physics of the collision process. The situation is analogous to the variational method, which provides a framework, but does not in and of itself provide a good approximation to the ground state. The quality of the variational result depends on the quality of the trial function used: how well it embraces the physics of the electronic motion.

Atom-atom or atom-molecule collisions are most often treated within the framework of the classical trajectory approximation; the nuclear motion is treated classically, while the electronic motion is treated quantum mechanically. The electronic state evolves from a time-varying Hamiltonian as the nuclear charges move along a classically determined trajectory. The study of electronic excitation in such collisions requires the solution of the time-dependent Schrödinger equation for the time-varying coefficients of a set of quasimolecular electronic states, which are here taken to be the diabatic states just discussed. We write

$$\Psi = \sum_n a_n(t)\psi_n(\mathbf{r};\mathbf{R}(t))\exp - i\int^t E_n(\tau)d\tau \ , \tag{7}$$

where

$$H_D\psi_n = E_n\psi_n \ . \tag{8}$$

The equations of motion for the coefficients $a_n(t)$ are obtained by substituting the expression (7) for Ψ into the time-dependent Schrödinger equation:

$$\left\langle \psi_m \left| H - i\frac{\partial}{\partial t} \right| \Psi \right\rangle = 0 \ . \tag{9}$$

The resulting equations are

$$\dot{a}_m = -\sum_n (iH'_{mn} + \langle \psi_m | \dot{\psi}_n \rangle) a_n \exp i\int^t (E_m - E_n)d\tau \ . \tag{10}$$

These equations are exact; no approximations have been made and H' does not have to be small.

III. THE TOPOLOGICAL PROJECTION OPERATORS

A. Introductory remarks

The formulation of the diabatic Hamiltonian described in the preceding section does not depend upon the specific projection operators used. The formulation merely provides a framework; the quality of the description of any given collision process depends entirely on how closely the projection operators employed embody the physics of that particular collision system. Different collision systems will call for different projection operators. This work will not attempt to cover all possibilities. Rather, it will focus on those cases in which near symmetry exists (e.g., near-inversion symmetry or near-reflection symmetry). The key characteristic of the wave function which the projection operators select out is the nodal structure of the wave function, in particular, the odd or even quality of the number of nodal surface intersections with any line or curve joining the centers. This is a topological feature which remains invariant under action of the diabatic Hamiltonian. The actual number of nodal surfaces is not an invariant of the diabatic Hamiltonian.

B. Projection operators in a nonorthonormal basis set

Before proceeding, a brief digression is in order concerning the definition of projection operators using a nonorthonormal basis set. To be useful, a formulation must be capable of being incorporated into a modern quantum-chemistry computer program, and these use a nonorthonormal basis set of Gaussian primitive elements about each nuclear center. Beyond mere utility, the Gaussian primitive basis sets are essential to the construction of the topological projection operators capable of selecting out a specified nodal structure.

Consider a finite dimensional subspace of Hilbert space spanned by a basis set on n linearly independent functions denoted by $|u_i\rangle = |i\rangle$, $i=1,\ldots,n$. The single index i denotes both the primitive element and the center about which that primitive element is defined. In most cases, the primitive elements will be Gaussian functions, although that is not essential to the formulation. The basis set could consist of Slater functions or atomic states. The overlap S_{ij} of the ith and jth basis elements is defined to be

$$S_{ij}=\langle i|j\rangle \; . \tag{11}$$

These overlaps form a nonsingular matrix S with inverse S^{-1}, the components of which are denoted by S_{ij}^{-1}. The essential property that makes an operator a projection operator is that of idempotency:

$$P^2=P \; . \tag{12}$$

In terms of the given basis set, it is easy to show that to satisfy the idempotency condition (12), P must be given by

$$P=\sum_{i,j=1}^{n} |u_i\rangle S_{ij}^{-1}\langle u_j| \; , \tag{13}$$

where S_{ij}^{-1} is a numerical coefficient multiplying the operator $|u_i\rangle\langle u_j|$. It is convenient (but not necessary) to place the coefficient between the two parts of the dyad to facilitate matrix multiplication. With P so defined,

$$\begin{aligned}
P^2 &= \sum_{i,j=1}^{n}\sum_{k,l=1}^{n} |u_i\rangle S_{ij}^{-1}\langle u_j|u_k\rangle S_{kl}^{-1}\langle u_l| \\
&= \sum_{i,j=1}^{n}\sum_{k,l=1}^{n} |u_i\rangle S_{ij}^{-1}S_{jk}S_{kl}^{-1}\langle u_l| \\
&= \sum_{i=1}^{n}\sum_{k,l=1}^{n} |u_i\rangle \delta_{ik}S_{kl}^{-1}\langle u_l| \\
&= \sum_{k,l=1}^{n} |u_k\rangle S_{kl}^{-1}\langle u_l| \\
&= P \; .
\end{aligned}$$

Thus it has been shown that P as defined by (13) is a projection operator. It projects onto the subspace spanned by the $|u_i\rangle$. Any state ψ which lies entirely within this subspace is of the form

$$\psi=\sum_{k=1}^{n} |u_k\rangle a_k \; .$$

Acting on such a state with P yields

$$\begin{aligned}
P\psi &= \sum_{i,j=1}^{n}\sum_{k=1}^{n} |u_i\rangle S_{ij}^{-1}\langle u_j|u_k\rangle a_k \\
&= \sum_{i,j,k=1}^{n} |u_i\rangle S_{ij}^{-1}S_{jk}a_k \\
&= \sum_{k=1}^{n} |u_k\rangle a_k \\
&= \psi \; .
\end{aligned}$$

Thus $P\psi=\psi$ for any state ψ that lies within the subspace. Conversely, any state ψ that is outside the subspace has the property $\langle u_j|\psi\rangle=0$ for $j=1,\ldots,n$. It therefore follows from the definition (13) of P that $P\psi=0$ for any state ψ outside the subspace.

C. Pseudoreflection symmetry

The $(\mathrm{HeH}_2)^+$ triatomic molecule provides an example of a near-reflection symmetry. The molecular energy surface is a function of the three variables r, R, and γ illustrated in Fig. 1. The electronic states and energies for this system have been calculated *ab initio* using the BRLJHU quantum-chemistry program.[19] For all values of γ, the electronic Hamiltonian is symmetric with respect to reflection in the plane containing the three nuclei. This is a true symmetry, denoted by C_s. All of the states considered in this work have positive C_s symmetry; hence this will be understood and not included in the state designations. In addition, when γ is exactly equal to 90°, the molecular geometry is that of an isoceles triangle, and the electronic Hamiltonian has an additional symmetry in a plane perpendicular to that of the nuclei and containing the bisector of the H-H separation, $\mathbf{r}$ (the y-z plane of Fig. 1). When this is the case, the electronic states have even symmetry [the solid curves in the energy diagram shown in Fig. 2(c)], or odd symmetry [the dot-dot-dashed curve in Fig. 2(c)]. Curves of different symmetry are clearly seen to cross. When γ is not exactly equal to 90°, the even-odd symmetry breaks down. However, near 90°, one would expect approximate symmetries to hold. The dashed curves of Fig. 2(b) show the *adiabatic* molecular energies for $\gamma=60°$, which clearly show avoided crossings. These are the calculations actually made by the BRLJHU program. As will be discussed below, quantum-chemistry programs for technical reasons do not yet allow diabatic states to be calculated. All diabatic energies have been obtained by interpolation, omitting those points for which diabatic nodal structure breaks down, and including only those adiabatic energy calculations for which the nodal structure shows clear diabatic behavior. The energies of the diabatic orbitals, as determined by the orbital characters, are shown as the solid or dot-dot-dashed curves in Fig. 2(d), and bear a close resemblance to the 90° case. As was pointed out in Ref. 10, the characters of the respective adiabatic molecular orbitals can be easily seen in the nodal structures, shown in Fig. 3, of the four lowest-energy orbitals obtained in the multiconfiguration *ab initio* calculation of adiabatic electronic states of $(\mathrm{HeH}_2)^+$. The orbitals are shown arranged in order of increasing energy, the first being the ground state. The diabatic crossing at $R=1.1$ a.u. of Fig. 2(d) is clearly seen in the nodal structure of the second and third adiabatic orbitals of Fig. 3, which interchange character in a narrow interval around $R=1.1$ a.u. In Figs. 3(a) and 3(b), the wave function for the second orbital has opposite sign on the two protons and small value at the He nucleus. The nodal surface lies between the two protons. In the case of 3(a), exact reflection antisymmetry holds, with eigenvalue -1. For 3(b), only pseudoantisymmetry holds, with eigenvalue -1 of the pseudoreflection operator. In Fig. 3(c), the adiabatic nodal surface does not exhibit any diabatic nodal structure. This is the avoided crossing region of the second and third diabatic orbitals, but pseudoantisymmetry is again seen in the *third* orbital of Fig. 3(d)–3(g). Proceeding in the reverse direction, the nodal surface of the second orbital of *g*, *f*, and *e* lies between the He and the H_2. This nodal structure breaks down in *d*, *c*, and *b*, to reestablish itself as the fourth orbital in 3(a). This orbital thus crosses two orbitals. Orbitals of pseudosymmetry eigenvalue $+1$ are shown by solid curves in Figs. 2(d) and 3, while those of pseudosymmetry -1 are shown by dot-dot-dashed curves, consistent with the notation used at $\gamma=90°$. For these orbitals, the coefficients multiplying corresponding Gaussians centered on the respective hydrogen nuclei are found to be either nearly equal ($+1$ pseudosymmetry) or nearly opposite (-1 pseudosymmetry). The *g* or *u* designation of the orbital labels in Fig. 2 will be discussed in Sec. III D below. In the pseudocrossing region, where the adiabatic orbitals do not exhibit definite character, the nodal surfaces are shown as dashed curves, consistent with Fig. 2.

The construction of the pseudosymmetry projection operators requires a basis set. Consistent with the goal of

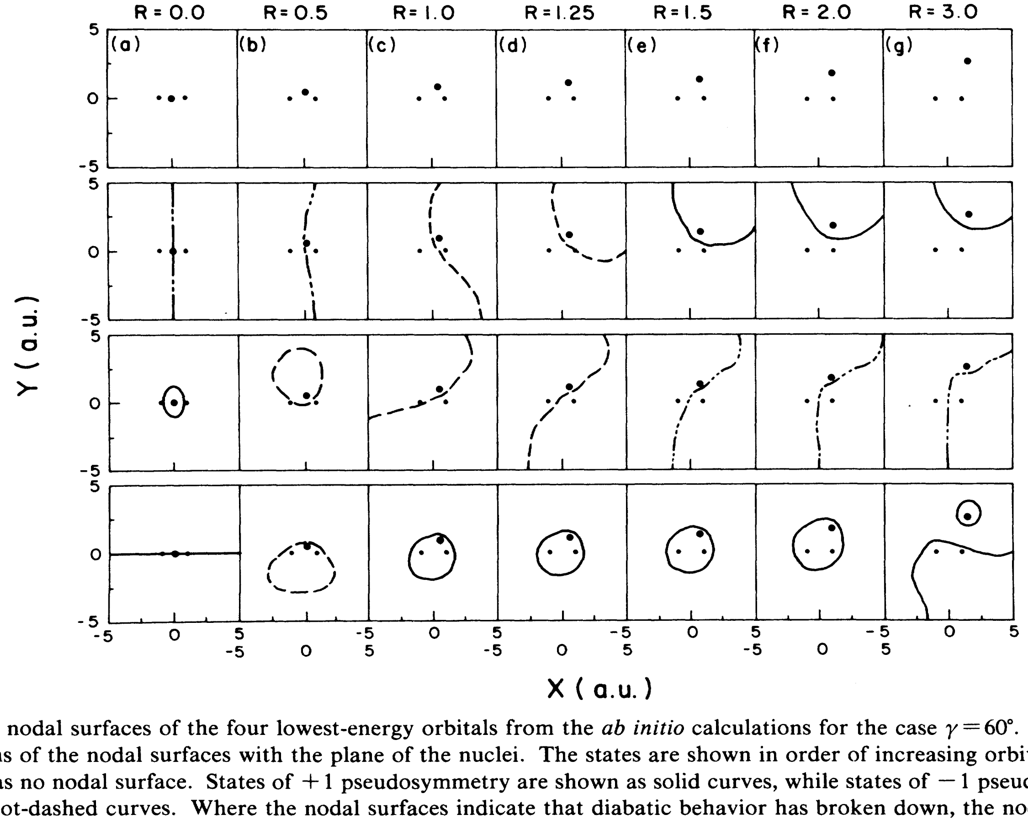

FIG. 3. The nodal surfaces of the four lowest-energy orbitals from the *ab initio* calculations for the case $\gamma=60°$. Actually, these are intersections of the nodal surfaces with the plane of the nuclei. The states are shown in order of increasing orbital energy. The ground state has no nodal surface. States of $+1$ pseudosymmetry are shown as solid curves, while states of -1 pseudosymmetry are shown as dot-dot-dashed curves. Where the nodal surfaces indicate that diabatic behavior has broken down, the nodal surfaces are shown as dashed curves.

this work to eventually incorporate the formulation into a quantum-chemistry program, the basis functions will be described in terms of Gaussian functions (or contractions thereof) centered on the H nuclei at A and B and on the helium nucleus at C. The He functions are denoted by g_{is}, g_{ix}, and g_{iy}, respectively, for s type, p_x type and p_y type. For all the states under consideration, there is no p_z component. The H functions are denoted by g_{ia} and g_{ib}. The index i serves to enumerate the functions of the primary set. The set used in this work consists of 24 functions: four s type, two p_x type, and two p_y type about each center; hence i runs from one to 24. (The basis set actually used in the *ab initio* calculations also included six p_z type Gaussians about each center. The amplitudes of these p_z functions came out identically zero for the states here discussed, as is to be expected for Σ states. Hence, these functions have been omitted from the enumeration.) To simplify the notation, p_x Gaussian primitive elements on proton B are given the opposite sign from those on A, in order that each transforms into the other (without sign inversion) upon reflection.

The primary functions are not themselves suitable as the basis set for the projection operators. The basis set will be defined in terms of linear combinations of Gaussians on A and B which have the same exponent. We write

$$\begin{aligned} g_{i+} &= g_a(\alpha_i)+g_b(\alpha_i) \ , \\ g_{i-} &= g_a(\alpha_i)-g_b(\alpha_i) \ . \end{aligned} \tag{14}$$

For example,

$$\begin{aligned} g_{3+} &= e^{-0.33r_A^2}+e^{-0.33r_B^2} \ , \\ g_{17-} &= e^{-0.33r_A^2}-e^{-0.33r_B^2} \ , \end{aligned}$$

where the enumeration lists the 14 states of positive pseudosymmetry first. The basis elements g_{i+} and g_{j-} are mutually orthogonal, but neither are orthogonal to the helium functions. Because the projection operators are required to be complementary, the construction of mutually orthogonal spaces is necessary for the two different pseudosymmetries. An intermediate basis set ϕ_i is first constructed:

$$\begin{aligned} \phi_{i+} &= \{g_{1+}, \ldots, g_{8+}, g_{9s}, \ldots, g_{12s}, g_{13p_y}, g_{14p_y}\} \ , \\ \phi_{i-} &= \{g_{15-}, \ldots, g_{22-}, g_{23p_x}, g_{24p_x}\} \ . \end{aligned} \tag{15}$$

The states ϕ_{i+} form a basis set for the subspace of pseudosymmetry $+1$. We write

$$|i+\rangle = u_{i+} = \phi_{i+} \ . \tag{16}$$

On the other hand, the ϕ_{i-} are not yet the final functions. Although they span a space of pseudosymmetry -1, that space is not orthogonal to ϕ_+ space. With the basis set (15), a set of projection operators g, p and r are defined. These projection operators are denoted by lower case letters, because they are single-particle projection operators, which project an orbital, not an entire multielectron state. Upper case notation is reserved for multielectron projection operators. We write

$$g = \sum_{i,j=1}^{24} |\phi_i\rangle s_{ij}^{-1} \langle \phi_j| \ , \tag{17a}$$

$$p = \sum_{i,j=1}^{14} |\phi_{i+}\rangle (s_p^{-1})_{ij} \langle \phi_{j+}| \ , \tag{17b}$$

$$r = \sum_{15}^{24} |\phi_{i-}\rangle (s_r^{-1})_{ij} \langle \phi_{j-}| \ . \tag{17c}$$

The projection operators g, p, and r are all of the form (13); they differ only in which basis functions are included in the defining set. As a consequence, the overlap matrices are different. The projection operator g projects onto the entire subspace of single-particle function space used in the quantum-chemistry program; p projects onto the ϕ_{i+} subspace, and r projects onto the ϕ_{i-} subspace. Because these latter are not orthogonal to the helium functions, r and p are *not complementary*. The subspace in g complementary to p is given by

$$q = g - p \ . \tag{18}$$

Since p space is contained within g space, $pg = gp = p$, making

$$pq = p(g-p) = pg - pp = p - p = 0 \ .$$

Thus q is complementary to p; it is also idempotent. It projects onto that portion of ϕ_- space which is orthogonal to p space. It is the modification of r which is complementary to p. The basis elements of q space are $q\phi_{i-}$, which are linear combinations of ϕ_{i-} and all the ϕ_{i+}'s. These latter accomplish the subtraction of those components of each ϕ_{i-} which lie in p space. We write

$$|i-\rangle = u_{i-} = q\phi_{i-} \ . \tag{16'}$$

Because both p space and q space are finite dimensional,

$$p + q = g \neq 1 \ . \tag{19}$$

With these projection operators, the pseudosymmetry projection operators are given by

$$\begin{aligned} p_+ &= p \ , \\ p_- &= q \ . \end{aligned} \tag{20}$$

It has been earlier stated that current quantum-chemistry programs do not yet allow the calculation of diabatic states. The sticking point can be seen in Eq. (14), which requires the contraction of Gaussians on different centers. Currently, quantum-chemistry programs allow contraction (a linear combination with fixed and predetermined coefficients) only of Gaussians on a single center. It is for this reason that diabatic states could not be calculated in this work. The limitation is, however, not intrinsic to the quantum-chemistry programs, and the programs can be modified to accomplish this. The task will not be easy, because these programs are so large that no modification is easy.

D. Pseudoparity symmetry

In addition to reflection symmetry, physical systems can exhibit symmetry with respect to inversion in the origin, which is called parity symmetry. The eigenvalues of the parity operator are labeled g for *gerade* and u for *ungerade*. The electronic states of the H_2 molecule or the He_2 quasimolecule have exact parity symmetry. It was suggested by Dowek *et al.*[16] that the H_2 in the HeH_2 system behaves like a helium atom. This is rigorously true if the H-H separation $r=0$. To the extent that the equilibrium H-H separation could be considered small, the $(HeH_2)^+$ triatomic molecular ion would behave like a He_2^+ diatomic ion, exhibiting parity pseudosymmetry. If the Gaussian set centered on the helium nucleus consists only of s-type states, a mathematical description of such a state of affairs can be simply accomplished by further subdividing p into p_g and p_u. The basis set u_{ig}, for p_g is given by

$$u_{ig}=u_+(\alpha_i)+u_c(\gamma_i)\ , \tag{21a}$$

where α_i and γ_i indicate properly matched basis elements from the H_2 and He primitive elements. Similarly, p_u space has as basis set

$$u_{iu}=(1-p_g)[u_+(\alpha_i)-u_c(\gamma_i)]\ . \tag{21b}$$

In the more general situation, with both s-type and p-type Gaussians on the helium center, the basis set (21) for p_g space must be generalized. This will be done below, along with a generalization that takes into account the differences between a He orbital and a H_2 orbital. Figure 4 shows plots of the wave functions for the two lowest-energy orbitals for the case $r=2$, $\gamma=60°$, and $R=3.0$, calculated in a multiconfiguration calculation of $(HeH_2)^+$. Values of ψ are plotted as functions of x and y in the plane $z=0$ containing the three nuclei. The lowest-energy orbital exhibits some g-type characteristic, but it is predominantly a He orbital. The second exhibits some u type, but is predominantly a H_2 orbital. These characteristics can be seen in Fig. 4; the nodal structure can be seen even more clearly in Fig. 3(g). The orbitals do not exhibit strong g or u symmetry, because the He 1s orbital is considerably lower in energy than the ground-state energy of the H-H system. The electronic energy of the lowest orbital of H_2 rapidly decreases as the H-H separation decreases, and the He nucleus is a H-H with zero separation. Thus the two orbitals become more g or u as r approaches zero. On the other hand, Rydberg orbitals have large radii, compared to which the H-H separation is relatively small, and much better approximated by zero. Pseudoparity for the system can be encompassed by properly generalizing the basis set to allow for these orbital characteristics:

$$\begin{aligned} u_{ig}&=u_{is}+A_iu_{i+} \quad \text{if } u_{ia} \text{ is } s \text{ type}\ ,\\ u_{ig}&=u_{ip}-A_iu_{i-} \quad \text{if } u_{ia} \text{ is } p \text{ type}\ , \end{aligned} \tag{22a}$$

and p_u space has the basis set

$$\begin{aligned} u_{iu}&=(1-p_g)(B_iu_{is}-u_{i+}) \quad \text{if } u_{ia} \text{ is } s \text{ type}\ ,\\ u_{iu}&=(1-p_g)(B_iu_{ip}+u_{i-}) \quad \text{if } u_{ia} \text{ is } p \text{ type}\ . \end{aligned} \tag{22b}$$

A sign difference will be noticed between linear combinations involving s-type and p-type u_{ia}, which is due to the fact that both u_{ip} and u_- themselves change sign on inversion. The coefficients A_i and B_i must all be positive, and will approach unity for very diffuse Gaussians, which describe the active regions of Rydberg orbitals. These coefficients permit the g orbital to be made a predominantly He orbital, and the u orbital predominantly a H_2 orbital. On the other hand, the Rydberg orbitals, which are much more nearly degenerate, with have much better g or u symmetry. Thus the basis elements with diffuse Gaussians will have coefficients very nearly equal to unity. The coefficients A_i and B_i are determined by diagonalizing $u_{is}+A_iu_{i+}$ *for fixed i* with respect to the one-electron Hamiltonian containing the kinetic energy

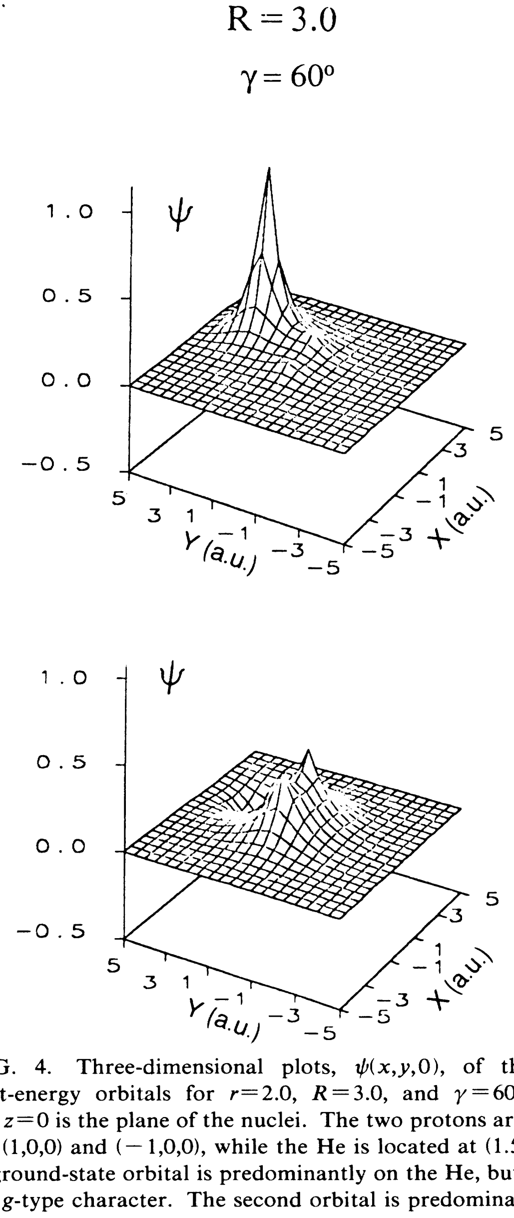

FIG. 4. Three-dimensional plots, $\psi(x,y,0)$, of the two lowest-energy orbitals for $r=2.0$, $R=3.0$, and $\gamma=60°$. The plane $z=0$ is the plane of the nuclei. The two protons are located at (1,0,0) and (−1,0,0), while the He is located at (1.5,2.6,0). The ground-state orbital is predominantly on the He, but shows some g-type character. The second orbital is predominantly on the H_2, but shows some u-type character.

and nuclear Coulomb potentials only. Two solutions will, of course, be obtained. The other solution is $B_i u_{is} - u_{i+}$, which appears in Eq. (22b). The situation is the same for the symmetry elements constructed from u_{ip} and u_{i-}.

E. Multielectron projection operators

Up to this point, only single-electron projection operators have been considered. In effect, these select out orbital types, while still allowing flexibility for the multiconfiguration quantum-chemistry program to adjust each orbital within the topological constraints imposed. However, orbitals do not occur in isolation but in multielectron Slater determinants called "configurations." The adjustment of the coefficients multiplying these configurations is done in the configuration-interaction (CI) part of the quantum-chemistry program. The diabatic formulation must also separate the configurations into disjoint subspaces, as described by Kubach *et al.*[9] This is accomplished by defining multielectron projection operators, a step that will lead to two new constants of the motion.

To simplify the presentation, the three-electron $(\mathrm{HeH}_2)^+$ system will be considered with only a single pseudosymmetry, leading to but a single pair of one-electron projection operators, for each set of electron coordinates: p_i and q_i. From these three pairs, eight products can be formed with either a p or a q for each electron (e.g., $p_1q_2q_3$). Each of these eight products is idempotent. For example,

$$(p_1q_2q_3)(p_1q_2q_3) = p_1^2q_2^2q_3^2 = p_1q_2q_3 \ .$$

Moreover, the eight products are mutually complementary. For example,

$$(p_1q_2q_3)(q_1q_2q_3) = (p_1q_1)q_2^2q_3^2 = 0 \ .$$

From these eight products, exactly four linear combinations can be constructed which commute with all permutation operators:

$$P_{\mathrm{I}} = p_1q_2q_3 + q_1p_2q_3 + q_1q_2p_3 \ , \tag{23a}$$

$$Q_{\mathrm{I}} = q_1p_2p_3 + p_1q_2p_3 + p_1p_2q_3 \ , \tag{23b}$$

$$P_{\mathrm{III}} = p_1p_2p_3 \ , \tag{23c}$$

$$Q_{\mathrm{III}} = q_1q_2q_3 \ . \tag{23d}$$

Consistent with the notation established in this work, the multielectron projection operators are represented by capital letters. The subscripts on P and Q denote how many single-electron projection operators of the given type make up the product terms. Because the eight product terms are idempotent and mutually complementary, it follows that the four operators defined in (23) are also idempotent and complementary:

$$P_J^2 = P_J, \quad Q_J^2 = Q_J \ , \tag{24a}$$

$$P_JP_K = P_JQ_K = Q_JP_K = Q_JQ_K = 0 \quad \text{for } J \neq K \ . \tag{24b}$$

It should be noted that these projection operators do not select out individual configurations; rather, they select out configuration *types*. There is still some CI flexibility within a given type.

The diabatic Hamiltonian for a crossing between a pq^2-type state and a p^3-type state is

$$H_D = P_{\mathrm{I}}HP_{\mathrm{I}} + P_{\mathrm{III}}HP_{\mathrm{III}} \ . \tag{25}$$

[Unfortunately, there are no examples of diabatic crossings of this kind among the lower levels of the $(\mathrm{HeH}_2)^+$ system.] Because of idempotency and complementarity, expressed in Eqs. (24), both P_{I} and P_{III} commute with H_D by exactly the same argument used to establish Eqs. (5). It therefore follows that

$$\pi_C = P_{\mathrm{III}} - P_{\mathrm{I}} \tag{26}$$

is a constant of the motion. Each of the crossing configuration types is an eigenfunction of π_C belonging to different eigenvalues:

$$\begin{aligned} \pi_C\psi_{p^3} &= +1\psi_{p^3} \ , \\ \pi_C\psi_{pq^2} &= -1\psi_{pq^2} \ . \end{aligned} \tag{27}$$

The diabatic Hamiltonian (25) can be easily extended to allow diabatic crossings of other configuration types:

$$H_D = P_{\mathrm{I}}HP_{\mathrm{I}} + P_{\mathrm{III}}HP_{\mathrm{III}} + Q_{\mathrm{I}}HQ_{\mathrm{I}} + Q_{\mathrm{III}}HQ_{\mathrm{III}} \ . \tag{28}$$

As a consequence, there are six configurational constants of the motion, of which only two are new,

$$\pi_C = P_{\mathrm{III}} - P_{\mathrm{I}} \ , \tag{29a}$$

$$\pi_{C'} = Q_{\mathrm{III}} - Q_{\mathrm{I}} \ . \tag{29b}$$

They describe two-electron diabatic crossings, denoted by DII in the usual nomenclature. The remainder, of the form $P_J - Q_K$, are already covered by the single-particle pseudosymmetry constants of the motion. The new configurational constants of the motion have no analogies among the true symmetries. In the example cited, the $(+1)(-1)^2$ configuration has a different configurational eigenvalue than does $(+1)^3$ (P_{I} as opposed to P_{III}), but has the same symmetry or pseudosymmetry. Thus this new diabatic constant of the motion is not a generalization of a point symmetry. For the actual Hamiltonian, one cannot invert or reflect the coordinates of one electron without simultaneously doing so to all. The interelectron repulsion energy $\sum i,j\, 1/r_{ij}$ is not invariant with respect to partial symmetry operations. As is the case with all diabatic constants of the motion, the new DII configurational constants of the motion are valid diabatic invariants only to the extent that the matrix elements of the interelectron potential term coupling different configurations is sufficiently small. A mathematical formulation cannot *a priori* establish anything about the real world; it can only provide a framework to mathematically describe what is observed in the real world.

F. Summary

The preceding sections have separately discussed three types of diabatic Hamiltonians each with a projection operator constant of the motion. All of them are relevant to the $(HeH_2)^+$ system. Two are extensions of well-known point symmetry invariants; the third depends on weak coupling between different configurations. All of these ideas can be simultaneously combined into a single diabatic Hamiltonian without interfering with each other. The required projection operators separate Hilbert space into disjoint subspaces.

G. Collisional excitation

The prototype diabatic energy levels of Fig. 2(d) suggest several predictions for electronic excitation in collisions of $H_2{}^+$ on He. Collisions of He^+ on H_2 require molecular calculations at $r=1.4$, and will be reported elsewhere. The ground state at $R=\infty$ is $H_2{}^+$ + He, each in its respective ground state. This is the $(1g+)^2(1u+)$ state. The first diabatic crossing at $R=1.1$, is between this state and the $(1g+)^2(1-)$, which separates as He + $H_2{}^+(1-)$. It will be recalled that among the lower-energy states, g states are predominantly He and u states are predominantly $H_2{}^+$ at modest values of R, and become pure as R approaches infinity. The $1-$ orbital of $H_2{}^+$ is the repulsive state, usually denoted by $1\sigma u$. Thus collisional dissociation is predict-

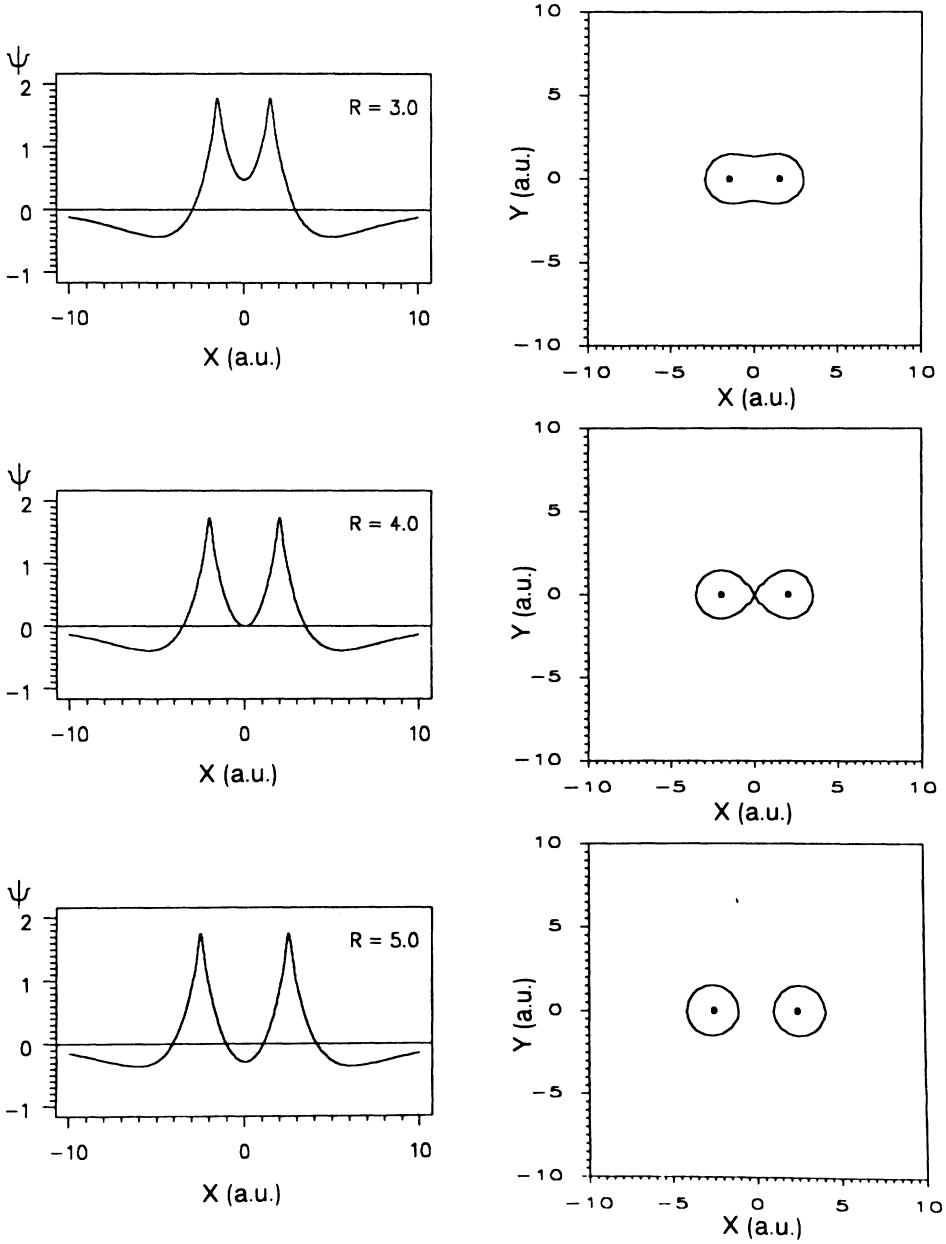

FIG. 5. Wave functions, $\psi(x,0,0)$ and nodal surfaces, $\psi(x,y,0)=0$, for a two-center system. This figure illustrates that the number of nodal surface intersections is not an invariant as the collisional separation R varies. What does remain invariant is the odd or even quality of the number of intersections of the nodal surfaces with any curve joining the centers.

ed. Because the $(1g+)^2(1-)$ diabatic state crosses the $(1g+)(1u+)^2$ level, charge exchange is also predicted. These outcomes could have been guessed by someone familiar with what avoided crossings look like in a molecular energy diagram, and were indeed discussed by Kubach *et al.*[9] and Hopper.[17] What would not be apparent is that the ground-state diabat also crosses the $(1g+)(2g+)(1u+)$, producing a Rydberg-excited He. This has not previously been expected. The Rydberg level crosses the $(1g+)^2(1-)$, giving a second possibility for ending up in the charge exchange channel. Thus the charge exchange channel could exhibit Rosenthal oscillations.

IV. RELATION TO OTHER WORK

The concept of a diabatic Hamiltonian defined in terms of topological projection operators just presented has drawn substantially from earlier works. Morse and Stueckelberg[11] implicitly suggest that the correlation diagram for a diatomic molecule can be understood in terms of a simplified independent particle model Hamiltonian, which is separable in prolate spheroidal coordinates. A discussion of the correlation diagram by these authors was in reality a discussion of diabatic states before that name was coined. Barat and Lichten[12] elaborated on this work, focusing on the nodal structure as the essential feature determining the character of the state. They define diabatic states in terms of the number of nodes on a line joining the two nuclei. In the present work, this concept was generalized to the topological structure of nodal surfaces[10] to extend the theory to molecules with more than two nuclei. O'Malley's suggestion[7,8] to define the diabatic Hamiltonian in terms of projection operators was grafted onto the thus extended formulation of Morse and Stueckelberg and Barat and Lichten by means of topologically defined projection operators, which are able to select out a given nodal structure as the molecular geometry is continuously varied.

One difference between the present work and that of Barat and Lichten is that the pseudosymmetry projection operators do not necessarily leave the number of nodes invariant; they only keep invariant the odd or even quality of the intersections of the nodal surfaces with a line joining the He nucleus with the H-H center. This is most clearly seen in the fourth orbital of the $(\mathrm{HeH}_2)^+$ system. The number of intersections of the nodal surfaces with this center-to-center line segment is either 2 or 0. As Fig. 5 illustrates, there is no discontinuity when two nodal surfaces touch and then coalesce into a single nodal surface, much the same as happens with soap bubbles. The number of intersections between the heavy black line joining the two centers changes from 0 to 2, both even. It is, however, impossible to change in a continuous way from an even number of intersections (which requires the sign of ψ to be the same on both centers) to an odd number of intersections (which requires the sign of ψ to be opposite).

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