Nonadiabatic effects in the collision of $F(2P)$ with $H_2(1\Sigma_g^+)$. II. Born-Oppenheimer and angular momentum coupling in adiabatic and diabatic representations

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The matrix elements necessary for the description of electronic interactions between the $1^2A'$, $2^2A'$, and $2^4A'$ surfaces of FH$_4$ are evaluated from Born-Oppenheimer states. It is shown that these couplings are handled most appropriately in a diabatic basis. The transformation between adiabatic and diabatic bases is explicitly obtained.

I. INTRODUCTION

We recently reported an ab initio Hartree-Fock (HF) computation of the three potential energy surfaces which correlate asymptotically with $H_2(1\Sigma_g^+) + \Xi(2P_{3/2,1/2})$. The study was undertaken to extend understanding of nonadiabatic effects in chemically reacting systems. The FH$_4$ system provides a useful test of the application of quantum-mechanical methods because of the availability of extensive experimental and theoretical information. With few exceptions, however, the theoretical investigations have assumed that reaction occurs on a single adiabatic potential energy surface. In the present paper, we focus on the determination of the coupling matrix elements required for a multisurface treatment of the collision dynamics in the FH$_4$ system where such matrix elements are expected to contribute significantly.

In Sec. II, the Born-Oppenheimer (BO) and angular momentum coupling matrix elements are derived and, the physical content of the numerical results is analyzed. Consistent with a pseudocrossing of the $1A'$ and $2A'$ surfaces at $R = 5.2$ a.u., the BO matrices reflect strong coupling in this region.

Section III describes the construction of a diabatic basis from the BO states. The diabatic basis greatly simplifies both the theoretical and numerical treatment of the scattering problem; instead of differential operators describing the kinetic coupling between the BO states, the diabatic states are coupled by nondiagonal terms of the potential matrix. Further, the diabatic basis makes it unnecessary to compute a large number of BO matrix elements and to follow their resonant type behavior in the pseudocrossing region. It also allows the prediction of some of the coupling matrix elements without calculating them from the electronic states. In the present case, this feature of the diabatic basis can be used to estimate electronic matrix elements of the operator $p_R = -i\hbar/\partial R$. Furthermore, in the diabatic basis the electronic angular momentum matrices possess a simple structure with essentially no $\theta$ dependence.

With the determination of the coupling matrix elements discussed in this paper and the availability of the potential surfaces (in the HF model) of Ref. 1, all of the significant information required for the study of multisurface interactions in collisions of $F$ with $H_4$ is specified.

II. MULTISURFACE INTERACTIONS FOR BO STATES

The total Hamiltonian of an atom A colliding with a molecule BC may be written (in the center-of-mass system with $\tilde{R} = \mathbf{r}$)

$$H = -\frac{1}{2\mu} \left( \frac{\partial}{\partial \tilde{R}} \right)^2 \tilde{R} + \frac{1}{2\mu \tilde{R}}$$

$$-\frac{1}{2m} \left( \frac{\partial}{\partial \xi} \right)^2 + \frac{N^2}{2m \xi^2} + H_{e1} + V_{\infty} + H_{\mu} \quad (1)$$

where $R$ is the intermolecular distance, $\xi$ is the BC distance, $I$ denotes the orbital angular momentum of the translational motion of $A$ relative to $BC$, and $N$ is the nuclear part of the molecule angular momentum of $BC$. The spin-orbit interaction $V_{\infty}$ will be explicitly considered in the present study, but other spin interactions and the mass polarization term $H_{\mu}$ are likely not important in FH$_4$ and will not be treated here. For $1\Sigma$ molecules, such as $H_2$ in its ground state, no distinction arises between nuclear and total rotational angular momentum.

Since all of the information on the electronic states is primarily obtained in a coordinate system attached to the molecular plane, it is advantageous to transform the operators $N^2$ and $I^2$ of Eq. (1) to the body-fixed frame. Introducing the total angular momentum $J = N + 1$ and the total electronic angular momentum $J = L + S$, where $L$ is the total orbital angular momentum and $S$ is the total spin angular momentum of the atom, one obtains

$$N^2 = \left[ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} - (\sin \theta)^2 (J_x - J_y)^2 \right] \quad (2)$$

$$I^2 = (J - J - N)^2$$

$$= (J - J)^2 - 2(J_x - J_y)^2 + N^2$$

$$+ 2 \cot \theta (J_x - J_y)(J_x - J_y) - 2(J_x - J_y) \frac{\partial}{\partial \theta} \quad (3)$$

Here $\theta$ is the angle formed by the $R$ and $\xi$ axes. The total angular momentum $J$ and its body-fixed components $J_x$, $J_y$, and $J_z$ depend on the Euler angles which specify the orientation of the molecular plane with respect to the space-fixed frame and thus do not act on the electronic functions. The couplings between electronic and nuclear motion may be classified as either BO, arising from the action of $p_R = -i\hbar/\partial R$, $p_I = -i\hbar/\partial I$.
\( \xi, \) and \( \theta_b = -i \alpha/\hbar \) on the electronic functions through their parametric dependence on \( R, \xi, \) and \( \theta, \) or Coriolis, involving electronic angular momenta in terms such as \( J \cdot J \) or \( J \times \mathbf{p}_b; \) see Eqs. (2) and (3). The spin-orbit interaction is given by \( V_{so} = g \mathbf{L} \cdot \mathbf{S} \) where, since further information is not presently available on this term, \( g \) is assumed to be \( R \) independent. In the remainder of this section, the numerical values of the BO coupling and angular momentum matrices are determined for the previously computed\(^4\) set of three SCF wavefunctions for \( \text{H}_2. \)

### A. BO matrix elements

Since the common symmetry of all nuclear arrangements for \( \text{H}_2 \) is \( C_2 \) (in the absence of spin-orbit interaction), the three energetically lowest BO states are \( ^3\Sigma^+ ', \ ^3\Pi^+ ', \) and \( ^3\Delta^+ ' \) and will be denoted in order by \( \varphi_{3}(R, \xi, \theta, \tau), \varphi_{2}(R, \xi, \theta, \tau), \) and \( \varphi_{1}(R, \xi, \theta, \tau). \) For any set of electronic functions \( \{\varphi_i(R, \xi, \theta, \tau)\}, \) the required matrix elements are

\[
\Pi_{ij}^a = \langle \varphi_i | p_a | \varphi_j \rangle,
\]

and

\[
\Pi_{ij}^b = \langle \varphi_i | \mathbf{p}_a \cdot \mathbf{r} | \varphi_j \rangle,
\]

where \( p_a = -i\hbar/\beta a \) and \( \alpha = R, \xi, \) or \( \theta. \) The elements \( \Pi_{ij}^a \) form a Hermitean matrix \( \Pi^a \) so that

\[
\Pi_{ij}^a = \Pi_{ji}^a^*,
\]

which for real functions \( \varphi \) leads to

\[
\Pi_{ii}^a = 0, \quad \Pi_{ij}^a = -\Pi_{ji}^a.
\]

The matrix \( \Pi^a \) is not Hermitean, but it is related to \( \Pi^a \) assuming completeness of the set \( \{\varphi_i\} \) by

\[
\Pi_{ij}^a = \sum_k \Pi_{ik}^a \Pi_{kj}^a + \langle p_a \Pi_{ij}^a \rangle.
\]

For real \( \varphi, \) the first term on the rhs of Eq. (8), i.e.,

\[
A_{ij}^a = \sum_k \Pi_{ik}^a \Pi_{kj}^a,
\]

leads to a real symmetric matrix while the second term

\[
B_{ij}^a = \langle p_a \Pi_{ij}^a \rangle
\]

defines a real antisymmetric matrix.

The evaluation of these matrix elements rests here on numerical differentiation of the wavefunctions. Defining an overlap matrix

\[
S_{ij}(\Delta \alpha) = \langle \varphi_i(\xi, \theta, r) | \varphi_j(\xi, \theta, r + \Delta \alpha, r) \rangle
\]

by integration over the electron coordinates \( r \) leads to

\[
S_{ij}(\Delta \alpha) = \delta_{ij} + \Pi_{ij}^a(\alpha) \Delta \alpha - \frac{1}{2} \Pi_{ij}^b(\alpha)(\Delta \alpha)^2,
\]

valid up to second order in \( \Delta \alpha. \) From the symmetry properties of \( \Pi^a \) and \( \Pi^{aa}, \) it then follows that

\[
[S_{ij}(\Delta \alpha)] + S_{ij}(\Delta \alpha) - 2S_{ij}(\alpha) = -A_{ij}^a(\alpha'),
\]

\[
[S_{ij}(\Delta \alpha) - S_{ij}(\Delta \alpha)]/(2\Delta \alpha) = \pm i B_{ij}^a(\alpha'),
\]

where \( \alpha', \alpha'' \) are values in the interval \( (\alpha, \alpha + \Delta \alpha). \)

Thus knowledge of \( S \) for one \( \Delta \alpha \) permits evaluation of \( \Pi^a \) and \( \Pi^{aa}. \) The increment \( \Delta \alpha \) must be chosen appropriately large to ensure numerical accuracy but sufficiently small to ensure that the computed matrix elements are representative for point \( \alpha. \) Once \( \Pi^a \) is known as a function of \( \alpha, \) the remaining antisymmetric contribution \( B^{aa} \) to \( \Pi^{aa} \) can be obtained in principle by numerical differentiation of \( \Pi^a. \) This step is not performed here, since (as shown in Sec. III) a diabatic representation can be found using numerical data on \( \Pi^a \) in which \( B^{aa} \) is transformed into a null matrix.

For \( \text{H}_2, S(\Delta \alpha) \) was computed for the three BO states. Table I lists the matrix element \( \Pi_{12}^a \) which completely specifies \( \Pi^a \) and the diagonal contributions to \( \Pi^{aa}. \) Non-diagonal symmetric elements of \( \Pi^{aa} \) are found to vanish. The results also show that the relations

\[
\Pi_{12}^{aa} = (\Pi_{12}^a)^2 + \Pi_{13}^{aa},
\]

and

\[
\Pi_{12}^{aa} = \Pi_{11}^{aa},
\]

hold and further that \( \Pi_{13}^{aa} \) is nearly \( R, \theta \) independent.

The term \( \Pi_{12}^{aa} \) is a contribution that is determined by the

### Table I. \( \theta \)-type BO matrices for \( ^3\Sigma^+ ', ^3\Pi^+ ' \) and \( ^3\Delta^+ ' \) states of \( \text{H}_2. \)

| \( \theta \) | \( \Pi_{12}^a \) | \( \Pi_{12}^{aa} \) | \( \Pi_{13}^{aa} \) | \( \Pi_{13}^{aa} \) |
|---|---|---|---|
| 3.5 | 0.235 | -0.150 | -0.698 | 0.22 |
| 30 | 0.038 | -0.101 | -0.097 | 0.05 |
| 60 | -0.103 | -0.109 | -0.009 | -0.11 |
| 90 | -0.122 | -0.110 | -0.097 | -0.11 |
| 4.0 | 0.370 | -0.231 | -0.095 | 0.37 |
| 30 | 0.037 | -0.097 | -0.095 | 0.04 |
| 60 | -0.151 | -0.118 | -0.095 | -0.15 |
| 90 | -0.173 | -0.125 | -0.095 | -0.18 |
| 4.5 | 0.676 | -0.554 | -0.094 | 0.63 |
| 30 | 0.600 | -0.154 | -0.095 | 0.06 |
| 60 | -0.371 | -0.233 | -0.094 | -0.32 |
| 90 | -0.253 | -0.108 | -0.094 | -0.26 |
| 5.0 | 0.228 | -0.509 | -0.094 | 2.20 |
| 30 | -0.275 | -0.171 | -0.094 | -0.24 |
| 60 | -0.372 | -0.233 | -0.094 | -0.32 |
| 90 | -0.253 | -0.108 | -0.094 | -0.26 |
| 6.0 | 0.132 | -1.383 | -0.094 | -1.10 |
| 30 | -1.281 | -1.746 | -0.094 | -1.28 |
| 60 | -0.773 | -0.773 | -0.094 | -0.82 |
| 90 | -0.634 | -0.498 | -0.094 | -0.64 |
| 8.0 | 0.693 | -0.378 | -0.094 | -0.67 |
| 30 | -0.900 | -0.900 | -0.094 | -0.97 |
| 60 | -1.230 | -1.616 | -0.094 | -1.25 |
| 90 | -1.169 | -1.245 | -0.094 | -1.12 |

Asymptotic limits for pure quadrupole-quadrupole interaction:

\[
\alpha \to 0: -0.667, -0.538, -0.094
\]

\[
\alpha \to 30: -0.855, -0.825, -0.094
\]

\[
\alpha \to 60: -1.244, -1.641, -0.094
\]

\[
\alpha \to 90: -1.143, -1.400, -0.094
\]

\(R \) in a.u., \( \theta \) in degrees, \( \Pi^a \) in \( \text{rad}^{-1} \) (in units of \( \sqrt{1} \)), \( \Pi^{aa} \) in \( \text{rad}^{-2} \).

\(b\) Computed from the diabatic Hamiltonian, see Eq. (25).
hydrogen molecular wavefunction only and merely reflects that this function follows the motion of the hydrogen nuclei as \( \theta \) changes which may be seen from the relation \( \psi_{1s} = (\psi_{1s})_1 | z_1 \rangle \psi_{1s}, \) cf. Eq. (18). Thus Eq. (15) essentially shows by comparison with the more general result, Eq. (8), that instead of having to sum over a complete set of intermediate states, it is sufficient to consider only those states within the manifold of the three BO states. It should also be mentioned that a simple model justifying relations (15) and (18) can be based on forming the BO states as products of adiabatically changing fluorine atom functions and the hydrogen molecular wave function. In Sec. III it will be shown that the numerical results obtained here for \( \Pi^g \) and \( \Pi^{ag} \) are sufficient to derive \( \Pi^f \) and \( \Pi^{ag2} \). The remaining BO matrices \( \Pi^f \) and \( \Pi^{ag2} \) will not be considered further since as discussed in Ref. 1, changes in \( \xi \) are felt to be unimportant for the range of geometries considered here.

B. Matrix elements of the angular momentum operators

Matrix elements of \( L_x, L_y, L_z, L_x^2, L_y^2, \) and \( L_z, \rho \) have been computed using standard methods to evaluate matrix elements between determinantal wavefunctions. Since all electronic coordinates are referred to the nuclear center of mass of the FHF system, it is necessary to discuss first their asymptotic behavior. Asymptotically the most natural choice would be different coordinate systems for F and HF, but in order to write the HF matrix elements in this region as sums of F and HF contributions, one must evaluate these latter matrix elements in the common coordinate system of FHF. Since, for example, in the definition of \( L_x \)

\[
L_x = -i \sum_x \left( \frac{\partial}{\partial z_x} - \frac{\partial}{\partial y_x} \right),
\]

(17)

the choice of origin enters through the electronic coordinates \( y_x \) and \( z_x \), the matrix elements of the separate species may in general be functions of \( R \) and \( \theta \). For a single hydrogen function \( \psi_{1s} \) one thus obtains

\[
\langle \psi_{1s} | L_x | \psi_{1s} \rangle = 0,
\]

\[
\langle \psi_{1s} | L_y | \psi_{1s} \rangle = 0.09395 \sin^2 \theta,
\]

\[
\langle \psi_{1s} | L_z | \psi_{1s} \rangle = 0.09395 \sin^2 \theta + 1.36878 R^2 - 0.21042 R^4 \sin^2 \theta,
\]

\[
\langle \psi_{1s} | L_z \rho | \psi_{1s} \rangle = 0.09395
\]

(18)

\[
\langle \psi_{1s} | L_z \rho | \psi_{1s} \rangle \Pi^{ag} = 0.09395.
\]

The expression in the last line, which is valid for \( R = 0 \), has been included here to point out the connection with \( \Pi^{ag} \).

The corresponding relations for the F-atom functions can be derived from the standard matrix representations for \( L_x, L_y, \) and \( L_z \) in cartesian form (denoted by \( L_x^f, L_y^f, \) and \( L_z^f \)) by rotating these matrices by the angle \( \theta_{HF} \) formed by the direction of the open shell fluorine orbital and the \( R \) axis in the \( 1^2A' \) state of FHF (in the limit \( R \rightarrow \infty \), see Ref. 1). This rotation does not affect \( L_z^f \) which has the form

\[
L_z = -i \begin{pmatrix}
0 & -1 & 0 \\
1 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix},
\]

(19)

but does change \( L_x^f \), for example, which is now given by

\[
L_x^f = -i \begin{pmatrix}
0 & 0 & \cos \theta_{HF}
0 & 0 & \sin \theta_{HF}
-\cos \theta_{HF} & \sin \theta_{HF} & 0
\end{pmatrix},
\]

(20)

From \( \theta_{HF} \) is a function of \( \theta \).

The matrices for the quadratic operators are

\[
L_{x^2} = L_z^f \cdot L_x^f,
\]

\[
L_{y^2} = (2 + 1.07775 R^2) I,
\]

\[
L_{z^2} = L_z^f \cdot \Pi^f.
\]

(21)

Here, for example, \( L_{x^2} \) denotes the \( 3 \times 3 \) matrix of the operator \( L_x^2 \). Similar notation is used for the other angular momentum operators, writing in particular \( L_{zg} \) for the matrix of \( L_z \rho \).

The nonvanishing terms of Eq. (18), the BO matrix elements \( \Pi^{ag} \) and

\[
\langle \psi_{1s} | \rho | \psi_{1s} \rangle = 0.473958 + 0.21042 \sin^2 \theta,
\]

(22)

and the term proportional to \( R^2 \) in \( L_z^2 \) of Eq. (21), are artifacts of the coordinate system used but will of course appear in matrix element computation. Such coordinate-system-dependent terms only lead to a constant shift in the Hamiltonian of Eq. (1) which of course has no bearing on the physical situation. In the present study, in which the angular momentum matrices have been computed from wavefunctions, these coordinate-system-dependent contributions can be subtracted by making use of their analytical representations and only the physically meaningful component of them retained without loss of generality. Since the diabatic representation derived in Sec. III will enable us to represent the angular momentum matrices in a concise form, no tabulation of these matrices for the pertinent BO states is given here. If wanted, they can be obtained from the diabatic matrices of Table II by applying the inverse transformation that defines the diabatic representation [see Eq. (23)].

III. TRANSFORMATION TO A DIABATIC BASIS

In situations where significant couplings between nuclear and electronic motion occur, the advantage of a diagonal electronic Hamiltonian for the BO states is at least compensated by the disadvantage of being compelled to treat the BO coupling terms. It is, therefore, of interest to consider other sets of functions which means in practice to find a unitary transformation that relates these alternative functions to the BO states. A diabatic basis of electronic functions is one such set and is by definition one in which couplings introduced through the kinetic energy operator vanish or at least become small. For this choice of basis, the electronic Hamiltonian is no longer diagonal.

It was shown in Sec. II A that significant BO coupling
TABLE II. Estimates of radial derivatives for the diatomic states (\(\theta = 0\)).

<table>
<thead>
<tr>
<th>(R)</th>
<th>(R_{11}^{JR})</th>
<th>(R_{22}^{JR} - R_{22}^{SR})</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.75</td>
<td>-0.49</td>
<td>-0.40</td>
</tr>
<tr>
<td>4.25</td>
<td>-0.47</td>
<td>-0.43</td>
</tr>
<tr>
<td>4.75</td>
<td>-0.47</td>
<td>-0.44</td>
</tr>
<tr>
<td>5.10</td>
<td>-0.55</td>
<td>-0.52</td>
</tr>
<tr>
<td>5.60</td>
<td>-0.37</td>
<td>-0.36</td>
</tr>
<tr>
<td>6.50</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>7.50</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

* Matrix elements are given in au. \(^{-1}\); the asymptotic value (-0.474) has been subtracted.

* Obtained by numerical differentiation of the \(\Sigma\) and \(\Pi\) wavefunctions.

* Mean value of interval used in differentiation; the interval length varied between 0.2 and 1 au.

As \(\theta\) increases, \(\theta_F\) becomes smoother until for \(\theta = \pi/2\), \(\theta_F\) equals \(\theta\) for all \(R\). This behavior in mind, the angle function \(\gamma\) of Eq. (23) is set equal to \(\theta_F\) and, as will be shown, this choice satisfies Eq. (25) for \(\sigma = \theta\).

Note that the complicated behavior of \(\theta_F\), together with the limited number of values obtained in the present study, prevent an immediate numerical differentiation of \(\theta_F\). Therefore, \(\theta_F\) is first related to functions with smooth behavior by performing the transformation (23) on the electronic Hamiltonian. The transformed Hamiltonian is given by its matrix elements

\[
H_{i,j} = \langle x_i | H_{el} | x_j \rangle \quad i, j = 1, 2, 3,
\]

and is related to the BO energies \(E_j(R, \xi, \theta)\) and the angle function \(\theta_F\) by

\[
E_j = \frac{1}{3} \left( (H_{11} + H_{22}) + (-)^{j+1} \left( (H_{11} - H_{22})^2 + 4 H_{12} H_{21} \right) \right) \quad j = 1, 2
\]

\[
E_3 = H_{33}
\]

\[
\tan 2\theta_F = 2H_{12} / (H_{11} - H_{22}).
\]

The matrix elements \(H_{i,j}\) are found to be slowly varying functions of the nuclear coordinates. Their \(\theta\) dependence is well represented by expansions in associated Legendre functions \(P^m_n(\cos \theta)\) with a fixed \(m\) value for a specific \(H_{i,j}\). This includes as a special case the common expansion of the intermolecular potential in Legendre polynomials. The use of \(P^m_n(\cos \theta)\) is suggested by the analytical form of the matrix elements \(H_{i,j}\) in limiting situations (e.g., at long range) and in general the \(m\) values are simply related to the structure of the diatomic Hamiltonian. In the present case, \(m = 0\) is sufficient for \(H_{11}\) and \(E_1\). The functions \(P^m_n(\cos \theta)\) are used to approximate the \(\theta\) dependence of \(H_{12}\), observing that both quantities are antisymmetric with reflection about \(\pi/2\), i.e.,

\[
H_{12}(\pi - \theta) = -H_{12}(\theta),
\]

and vanish at \(\theta = 0, \pi/2\), and \(\pi\).

The analytical expression for \(H_{ij}\) can then be used to derive \(\theta_F\) and \(\theta_F \theta_F\) from Eq. (27) or similar relations for \(\sin 2\theta_F\) and \(\cos 2\theta_F\). As the last column in Table I shows, \(\theta_F \theta_F\) compares very well with \(-P^m_n\). Thus the basis \(\{x_i\}\) defined through \(\theta_F\) is clearly diabatic in the sense that \(\langle x_i | \theta_F | x_j \rangle\) vanishes.

For the operator \(\theta_F^2\), the transformation (23) and Eq. (25) are used to obtain

\[
\langle x_1 | \theta_F^2 | x_2 \rangle = (P^m_n)^2 + \cos \theta_F P^m_n + \sin \theta_F P^m_n
\]

\[
- \sin \theta_F \cos \theta_F (P^m_n + P^{m+n}_{n+1}) + (P^m_n + P^{m-n}_{n-1}),
\]

\[
\langle x_2 | \theta_F^2 | x_1 \rangle = \theta_F P^m_n + \sin \theta_F \cos \theta_F (P^m_n - P^{m+n}_{n+1})
\]

\[
+ \cos \theta_F P^m_n - \sin \theta_F P^m_n P^{m-n}_{n-1},
\]

and similar expressions for \(\langle x_3 | \theta_F^2 | x_1 \rangle\) and \(\langle x_1 | \theta_F^2 | x_2 \rangle\).

Introducing Eqs. (15) and (16) found for the computed BO matrices shows that

\[
\langle x_i | \theta_F^2 | x_j \rangle = \delta_{ij} P^m_n \quad i, j = 1, 2, 3.
\]

The origin of the constant term \(P^m_n\) has been discussed earlier. Since it can be neglected without altering

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physical situation, Eq. (31) suggests the interpretation, see Eqs. (8) and (25),
\[ \langle x_i | p_{2k} | x_j \rangle = 0 \quad i = 1, 2, 3; \quad k = 1, \ldots, \infty. \]  
(32)

Thus the diabatic states of the manifold given by \( \{ x_i, \quad i = 1, 2, 3 \} \) have no coupling arising from \( p_{2k} \) to any other state inside or outside the manifold and are in effect \( \theta \) independent for a specific \( R \).

The diabatic basis has in addition the important property
\[ \langle x_i | p_{2k} | x_j \rangle = 0 \quad i, j = 1, 2, 3, \]  
(33)

which by symmetry holds for \( \theta = 0 \) and thus by
\[ p_{2k} \langle x_i | p_{2k} | x_j \rangle = p_{2k} \langle x_i | p_{2k} | x_j \rangle = p_{2k} \langle x_i | p_{2k} | x_j \rangle = \sum_k \left( \langle x_k | p_{2k} | x_i \rangle \langle x_k | p_{2k} | x_j \rangle \right) \]

holds for all \( R \) and \( \theta \) using Eq. (32). Estimates of the diagonal elements \( \langle x_i | p_{2k}^2 | x_i \rangle \) for \( \theta = 0 \) are given in Table II; nondiagonal terms vanish by symmetry. As expected for molecular states, the diabatic states change to a certain degree from their asymptotic limiting values as \( R \) decreases. The diagonal corrections \( \langle x_i | p_{2k}^2 | x_i \rangle \) should also be representative for \( \theta \neq 0 \) based on the \( \theta \) independence of the diabatic states inferred from Eq. (32).

Application of the diabatic transformation to the angular momentum matrices of Sec. II B yields the results given in Table III. Not listed in Table III, but of importance are the matrix elements of \( L_x \) and \( L_z^2 \) which are found to be \( R \) and \( \theta \) independent and therefore equal to their asymptotic values. Thus the linear combinations of the diabatic states
\[ x^1 = 2^{-1/2}(x_3 + ix_2), \]
\[ x^0 = x_1, \]
\[ x^- = 2^{-1/2}(x_3 - ix_2), \]  
(35)

form a representation in which \( L_x \) and \( L_z^2 \) are diagonal. The matrix elements of \( L_x \) and \( L_z \) begin deviating from their asymptotic values at \( R \sim 4.5 \) a. u., and are only weakly \( \theta \) dependent.

The aim of the preceding development in this section has been to eliminate the BO couplings by a suitable choice of representation. The procedure described is also useful, however, for minimizing the amount of computation required to evaluate BO matrix elements. Once the diabatic basis is established by comparison of computed and derived BO matrix elements, it can be used to generate matrix elements in regions where they rapidly vary. In addition, the BO matrix elements of the operator \( p_{2k} \) resulted here from Eq. (25) without the need of wavefunction computations at additional geometries.

**IV. DISCUSSION**

It is clear that the construction of the diabatic basis used here is intimately related to the \( \theta \) dependence of the BO states. For the DIM approach,\(^{26}\) kinetic energy couplings of the BO states seem to be unimportant while in the collinear case,\(^{27}\) coupling by \( p_{2k} \) is nonexistent. Of course it would contradict the essence of the preceding discussion of diabatic states to perform a transformation to a set of abibatic states which diagonalize \( H_{ad} + V_{so} \) and in which the coupling between the electronic surfaces is effected by the nuclear kinetic energy as a result of the-coordinate dependence of the diagonalizing transformation.

In a scattering situation, it is convenient to factor the wavefunction corresponding to the Hamiltonian of Eq. (1) into a product of a nuclear and an electronic wavefunction and to choose asymptotically a diagonal representation for the operators \( N^2 \), \( P^2 \), and \( J^2 \). This diagonal structure is preserved for arbitrary \( R \) as long as the electronic angular momenta and the BO coupling arising from \( p_{2k} \) do not differ from their asymptotic values. Thus, from the vanishing of the \( p_{2k} \) coupling and the conservation of the component \( L_z \) in the diabatic representation, it can be concluded that no coupling remains for the operator \( N^2 \).

Homogeneous perturbations arising from \( p_{2k}^2 \) and \( L_z^2 \) have magnitudes \( \langle x_i | p_{2k}^2 | x_i \rangle / 2 \mu \) and \( \langle L_z^2 | -2/2\mu R^2 \rangle \), respectively, and lead to an insignificant modification of the effective molecular potentials. The angular coupling contained in \( P^2 \) is represented by \( (J - N) \Delta L / 2\mu R^2 \), denoting by \( \Delta L \) the deviation of \( L \) from its asymptotic value. For typical values of \( R \), this quantity is \( \sim 10^{-5} / J \) which is small for \( J \) values important in thermal energy collisions.

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*Matrix elements in units of \( \hbar = \sqrt{1/2} \). The diabatic functions \( x_1 \), \( x_2 \), \( x_3 \) transform for \( \theta = 0 \) as \( z, y, x \) resp.*

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**TABLE III. Angular momentum matrices of FH2 in diabatic representation.**

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<tr>
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<th>( R )</th>
<th>( \theta )</th>
<th>( L_z^2 = L_x^2 )</th>
<th>( L_z^3 )</th>
<th>( L_z^4 )</th>
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In contrast to the complexity of the various coupling terms for BO states, it has been shown here that the diabatic representation leads to a convenient treatment of \( \text{F} + \text{H}_2 \) collisions in terms of a nondiagonal potential matrix and a diagonal representation for the nuclear operators \( N^2 \) and \( P^2 \). A similar procedure for systems other than \( \text{FH}_2 \) should be applicable in cases where multiple surfaces arise from asymptotic degeneracies.

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\(^4\)F. Rebentrost and W. A. Lester, Jr., "Nonadiabatic Effects in the Collision of \( \text{F}^2P \) with \( \text{H}_2^1\Sigma^+ \): III. Scattering Theory and Coupled-Channel Computations" (in preparation)


\(^8\)P. O. Löwdin, Phys. Rev. 97, 1474 (1955).
