# Dressed Adiabatic and Diabatic Potentials To Study Topological Effects for F + H$_2$

A. Csehi,[†] A. Bende,[‡] G. J. Halász,[†] Á. Vibók,[§] A. Das,[∥] D. Mukhopadhyay,[∥] S. Mukherjee,[⊥] S. Adhikari,[⊥] and M. Baer*[,#]

[†]Department of Information Technology, University of Debrecen, H-4010 Debrecen, P.O. Box 12, Hungary

[‡]Molecular and Biomolecular Physics Department, National Institute for Research and Development of Isotopic and Molecular Technologies, 400293 Cluj-Napoca, Romania

[§]Department of Theoretical Physics, University of Debrecen, H-4010 Debrecen, P.O. Box 5, Hungary

[∥]Department of Chemistry, University of Calcutta, Kolkata 700 009, India

[⊥]Department of Physical Chemistry, Indian Association for Cultivation of Science, Jadavpur, Kolkata 700 032, India

[#]The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

**ABSTRACT:** We report here on the two lowest, rigorous-accurate diabatic potential energy surfaces (PES), for the F + H$_2$ system, as calculated by including the two dominant topological effects of this system at the low energy region, namely, the Jahn–Teller effect and the Renner–Teller effect. Both effects were treated in the most rigorous way as demanded by the Born–Oppenheimer approach. No approximations were made, and in those cases where convergence was required, it was satisfied. In other words, convergence was attained in all situations. The numerical part that includes the calculation of the two lowest ab initio adiabatic PESs and the corresponding nonadiabatic coupling terms (NACTs) was carried out using the MOLPRO program. The required diabatic potentials are calculated by employing these ab initio adiabatic PESs and the corresponding adiabatic-to-diabatic angles as obtained employing the above-mentioned ab initio NACTs. The relevance of these Renner–Teller/Jahn–Teller diabatic potentials is studied by comparing the dressed-lowest ab initio adiabatic PES and the one formed by diagonalizing the dressed-diabatic 2 × 2 potential matrix. The dressed-potentials are calculated employing the *vib-rotational* manifold derived for each of the three surfaces, namely, the lowest adiabatic potential and the two diabatic ones. This kind of study was recently recommended by Lipoff and Herschbach (*Mol. Phys.* **2010**, *108*, 1133) as a "blessed-practice" for the relevance of any PES. In the present case significant differences were revealed between the two types of dressed-adiabatic PESs, eventually, indicating that the lowest, ab initio PES (due to the Born–Oppenheimer approximation) is not adequate for low energy processes.
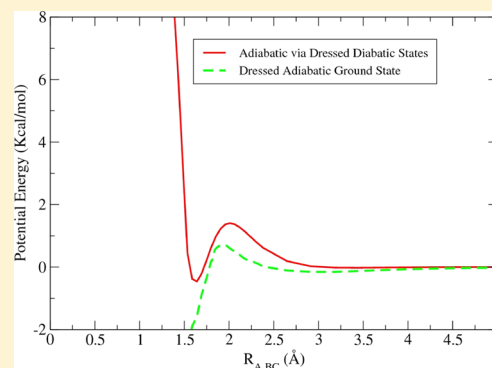
## I. INTRODUCTION

During the past few years numerous trials were made to find out to what extent topological effects really affect the lower Born–Oppenheimer (BO) adiabatic potential energy surfaces (PES). For instance, studies failed in showing such effects for the H + H$_2$ reactive system and its various isotopic equivalents[1–3] and we failed to show that in our recent topological studies as carried out for the HHF system.[4] We also failed, in part, while studying a two-dimensional reactive model:[5–7] Here whereas, the state-to-state reactive vibrational transitions were affected (sometimes even significantly) the total the probabilities (whether being nonreactive or reactive) were left intact.

Although we failed until recently to reveal any influence of topological effects on the F + H$_2$ system, we continued with our efforts in this direction.[8,9] Most of the odds are against this possibility. It is well-known that the existing BO lower adiabatic PES produces results that fit reasonably well the known

relevant experimental results ranging from the temperature dependent rate constants up to the energy dependent, most sensitive, differential cross sections. It is also well-known that this system possesses Jahn–Teller (JT) conical intersections (ci),[10–12] formed by the four lower states 1A′, 2A′, 3A′, and 4A′, which are located at three different points along the minimum energy path of the reagents channel. Hence, if a system is supposed to be affected by JT-cis, this system looks promising in this sense at least.

Recently, we published the two lower JT-diabatic PESs for this system.[4] To do that, we employed the angular nonadiabatic coupling term (NACT) $\tau_\varphi(\varphi,q|r) = \langle \chi_1(\varphi,q|r)|(\partial/\partial\varphi)\chi_2(\varphi,q|$

$r)\rangle$ (see Figure 1 for the coordinates) to calculate the required adiabatic-to-diabatic-transformation (ADT) angle $\gamma_{12}(\varphi,q|r) =$
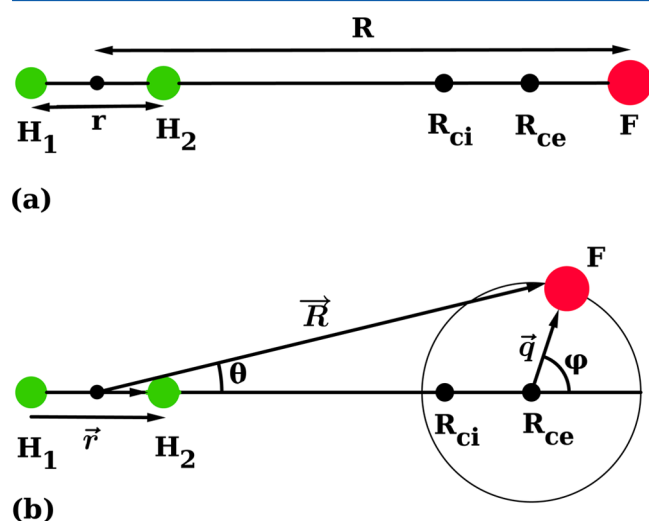


**Figure 1.** Schematic picture of the system of coordinates and various points of locations. (a) The point of (1,2) $ci$ is at $R_{ci}$, the center of all circular contours is at $R_{ce}$. Also shown are the positions of the three atoms along the collinear axis. (b) Two spherical systems of coordinates: $(R, \theta|r)$ and $(\varphi, q|r)$ used throughout the study.

$\int_0^\varphi \tau_{12}(\varphi',q|r)\, d\varphi'$, which is used to form the $2 \times 2$ ADT matrix, $\mathbf{A}(\varphi,q|r)$. Next, this matrix is applied to calculate the *diabatic* PES, namely, $\mathbf{W}(\varphi,q|r) = \mathbf{A}(\varphi,q|r)\,\mathbf{u}(\varphi,q|r)\,\mathbf{A}^*(\varphi,q|r)$.[13] Here $\mathbf{u}(\varphi,q|r)$ is a diagonal matrix that contains the *adiabatic* PESs. These NACTs are expected to yield meaningful diabatic PESs if and only if they satisfy the following quantization rule

$$\alpha(q|r) = \int_0^{2\pi} \tau_\varphi(\varphi',q|r)\, d\varphi' = n\pi \tag{1}$$

(where $n$ is an integer) along any circle, with a given radius $q$, in the region of interest.[14,15] The angle $\alpha(q|r)$ is also sometimes identified with the Pancharatnam–Berry phase. Unfortunately, the NACTs that MOLPRO supplied in this case were quantized only along circles with small radii (3 au > $q$ in case the center of the circles, was at, or close to, the point of the (1,2)$ci$; see Figure 1). Thus, for most of the region of interest, the above quantization does not hold and we had to find ways to correct for this mishap. Such a correction, based on symmetry arguments, was worked out (by employing complementary line integrals[11]) and the corresponding single-valued diabatic potentials were formed accordingly.

To find out whether the JT-$ci$ really has any effect on the lower BO adiabatic PES, we compared ordinary dressed-*adiabatic* potential *curves* with *adiabatic* curves formed via dressed-*diabatic* potential curves, both calculated as a function of the reagents' translational coordinate $R$.[4] The dressed potentials were formed not by applying the whole vib-rotational (internal) manifold (as should have been done) but only by employing the corresponding rotational manifold. Because only minor deviations were noticed,[4] the conclusion was made that the (1,2) JT-$ci$ is expected to have at most a mild effect on what happens along the entrance arrangement channel while the fluorine atom interacts with the hydrogen molecule. This probably applies to cold reactions as well.

Following that study we concluded that a last resort for the topological effects in molecular systems is to incorporate the Renner Teller (RT) effect in the calculations.[8,9] The RT effect is created by two $\Pi$ states, 1A' and 1A", usually the two lowest states in this system. It is formed at degeneracy points known to be solely located along the *collinear axis*! Because the (1,2) JT $ci$ is located on the same axis for any HH distance, $r$ (Figure 1) a JT-seam is encountered as a function of $r$. Consequently, a situation is formed where the two seams intersect each other for any $r$-value. Until recently,[8,9] these two effects were *never* included in a single numerical study; thus doing it increases the prospects of finally revealing the topological effects. Indeed, some positive hints in this direction were revealed already in ref 8 where, like earlier,[4] a treatment employing only the *rotational* manifold, was carried out.

In this article we follow a suggestion by Lipoff and Herschbach[16,17] and report on an extensive comparison between two dressed-*adiabatic* potential energy curves (a) the one that follows directly from the lowest BO surface and (b) the one produced by the dressed-RTJT *diabatic* $2 \times 2$ potential energy matrix (all calculated as a function of the reagents translational coordinate $R$). It is important to emphasize that the dressed-potentials (the pure adiabatic ones and the corresponding diabatic ones) are formed employing the complete vib-rotational manifold as, indeed, recommended by Lipoff and Herschbach.[16–18]

## II. COMMENTS

(a) In what follows we refer to the situation just described as the Renner–Teller/Jahn–Teller (RTJT) effect.

(b) It is important to emphasize that the JT effect is formed between two states of the same symmetry (usually designated as 1A' and 2A', etc.) whereas the RT effect is formed between two states of different symmetry (usually designated as 1A' and 1A", etc.)

(c) In the present study, just like in our recent studies,[4,8,9,11] we do not include the spin–orbit (SO) coupling (such calculations were reported, e.g., in refs 21 and 22). It is very likely that as long as this coupling is ignored the corresponding *dynamic* calculations are not trustful, but our main concerns at this stage are the BO adiabatic and diabatic potentials and not the dynamic calculations per se.

## III. THEORETICAL BACKGROUND

In our previous publications we discussed two approaches to form diabatic potentials. Both are based on deriving ADT angles from Born–Oppenheimer NACTs.[23–25] In the first approach the ADT angles were based on one NACT, $\tau_{12}(R,\theta|r)$, that couples the two lower adiabatic states, i.e., 1A' and 2A', which are associated with one of the $\Pi$-states and the $\Sigma$-state. This approach was found to be troublesome as the resulting ADT angles were not quantized, thus leading to ill-defined diabatic PESs. As a result these ADT angles were modified by employing complementary line integrals to guarantee the desired quantization feature.[4,11] In the second approach (which is pursued in the present article) the ADT angles are based on two NACTs, namely, the previously mentioned $\tau_{12}(R,\theta|r)$ and $\tau_{11''}(R,\theta|r)$ which is a NACT formed by 1A' and 1A", the two (lower) $\Pi$-states.[8,9] To calculate the required $3 \times 3$ ADT matrix we employ the quasi-Euler angles.[26–34]

To treat a (general) tristate system by employing Euler angles, it is usually enough to calculate two Euler angles (instead of three angles as a general case may demand) that

fulfill the following two coupled first-order differential equations:[31,32]

$$\frac{\partial}{\partial\varphi}\gamma_{12} = -\tau_{12} - \tan\gamma_{13}(\tau_{23}\cos\gamma_{12} + \tau_{13}\sin\gamma_{12}) \tag{2a}$$

$$\frac{\partial}{\partial\varphi}\gamma_{13} = \tau_{23}\sin\gamma_{12} - \tau_{13}\cos\gamma_{12} \tag{2b}$$

These two equations are solved with the aim of calculating the, so-called, privileged ADT angle $\gamma_{12}(\varphi, q)$. The introduction of the *privileged* angle enables the extension of the earlier defined two-state topological phase, $\alpha_{12}$, to three-state systems or any other multistate system.[28,34] A straightforward choice for this purpose is the *end-of-the-contour* value of the angle $\gamma_{12}$. Thus, $\alpha_{12}(q) = \gamma_{12}(\varphi=2\pi, q)$.[31]

This recent development was exploited to study the tristate system made of the three lower states 1A′, 1A″, and 2A′. Following a detailed analysis,[8,9] it was established that whereas the 1A′ and 2A′ that originate from one of the Π-states and the Σ-state are coupled via a spiky ordinary smooth JT-NACT, the two states 1A′ and 1A″ that originate from the two degenerate Π-states are coupled via an RT-NACT. The reason for the appearance of the spiky NACT (spiky to the level that its shape becomes essentially a Dirac-δ function[35,36]) is the fact that any circular contour that surrounds the JT-ci intersects the collinear axis that happens to be a parabolic seam, namely, a line of parabolic intersections (more about this issue can be found in ref 9). The resulting equations to be solved are[9]

$$\gamma_{12}(\varphi) = \begin{cases} -\int_0^\varphi \mathrm{d}\varphi'\,\tau_{12}(\varphi') & 0 \leq \varphi \leq \pi \\ -\int_0^\varphi \mathrm{d}\varphi'\,\tau_{12}(\varphi') + \chi(\varphi=\pi) & \pi \leq \varphi \leq 2\pi \end{cases} \tag{3}$$

where $\chi(\varphi=\pi)$, a constant, is given in the form

$$\chi(\varphi=\pi) = -\eta\frac{\pi}{2}\tan\{\gamma_{13}^{(0)}(\varphi=\pi)\}\sin\{\gamma_{12}(\varphi=\pi)\} \tag{4}$$

Here

$$\gamma_{13}^{(0)}(\varphi) = -\eta\frac{\pi}{2}\cos\gamma_{12}(\varphi=\pi) \tag{5}$$

and $\eta$, the so-called, Renner−Jahn coupling term, is a pure number:[9]

$$\eta = \frac{2\sqrt{2}}{\pi} = 0.9003 \tag{6}$$

The features of the function $\chi(\varphi=\pi)$, which forms the abrupt down shift of $\gamma_{12}(\varphi, q)$ at $\varphi = \pi$, are discussed elsewhere[9] and here we just mention two of them: (1) Because the diabatic potentials have to be single-valued at every point in configuration space, they also have to be *so* at $\varphi = \pi$. Consequently, the value of $\chi(\varphi=\pi)$ has to guarantee the equality $\sin[\gamma_{12}(\varphi=\pi)] = \sin[\gamma_{12}(\varphi=\pi)+\chi]$ and a similar equality (up to a sign) for the cosine function. (2) Because the value of $\gamma_{12}(\varphi)$ at the end of the closed circular contour, namely, $\gamma_{12}(\varphi=2\pi)$ has to be equal to $n\pi$ ($n$ is an integer), the vertical shift, $\chi(\varphi=\pi)$, has to guarantee the following *quantization* condition:

$$\alpha(q) = -\int_0^{2\pi}\mathrm{d}\varphi'\,\tau_{12}(\varphi') + \chi(\varphi=\pi) = n\pi \tag{7}$$

where $\alpha(q)$, as mentioned earlier, is the *topological* phase. Vertical jumps of this type are known to exist when charge-transfer processes are studied.[37−39]

In Figure 2 are presented the (vertical) shifted (1,2) ADT angles, $\gamma_{12}(\varphi|q)$, as calculated according to the recipe in eqs
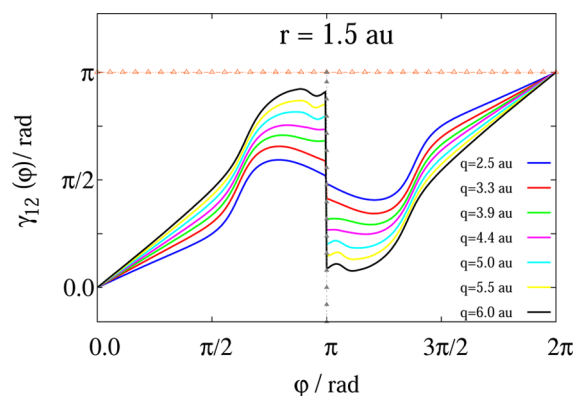


**Figure 2.** Adiabatic-to-diabatic-transformation (mixing) angle, $\gamma_{12}(\varphi|q)$, for circular contours at $R = R_{ce} = 6$ au along the interval $0 \leq \varphi \leq 2\pi$ as calculated by employing eq 2. The calculations were done for seven different circles with radii in the range: [2.5, 6.0 au]. All calculations were done for $r = 1.5$ au.

3−6 for the case that $r$ (the HH distance) equals 1.5 au. Curves for seven (7) $q$-values in the range 2.5< $q$ <6.0 au, are given. To form the below required PESs, we use $r$-values in the range 1.1 < $r$ < 2.5 au. The adiabatic potentials were calculated for a grid size of $\Delta r = 0.1$ au and the NACTs for a varying grid sizes (0.1 or 0.2 au). One fact has to be emphasized: In all cases the ADT angles used/presented in this article whether being unaffected (in case of contours with small radii) or shifted downward at $\varphi = \pi$ (in other cases) ended-up, following a closed contour, with a quantized topological phase $\alpha_{12}(q)$ (see eq 7), namely, becoming equal to $\pi$ when $\varphi = 2\pi$. At this stage we emphasize again that the downward shifts for the various cases were calculated according to eqs 4 and 5 where $\eta$, the theoretical magnitude, is given in eq 6. In other words no *artificial* fitting was done!

## IV. POTENTIAL ENERGY SURFACES

In this section we concentrate on dressed-potentials formed by the vib-rotational manifold that consists of three-dimensional nuclear vib-rotational eigenfunctions. The BO−dressed-*adiabatic* potentials $u_{a0}(R)$ is derived from the expression

$$u_{a0}(R) = |Z_{ak=0}(\theta, r|R)\rangle u_0(\theta, r|R)|Z_{ak=0}(\theta, r|R)\rangle \tag{8}$$

Here $u_0(\theta, r|R)$ (see Figure 1 for the coordinates) is the *lowest* adiabatic PES and $|Z_{ak=0}(\theta, r|R)\rangle$ is the corresponding (lowest) adiabatic vib-rotational nuclear eigenfunction calculated for this PES (see Appendix I).

For the diabatic case the vib-rotational eigenfunctions $|Z_{dk=0l}(\theta, r|R)\rangle$, $l = 1, 2$, are calculated by employing the corresponding diabatic PESs, $V_l(r, \theta|R) = 1, 2$ (see ref 9, Appendix B). Having these eigenfunctions we calculate the dressed-*diabatic* potential

$$\tilde{V}_{k=0l}(R) = \langle Z_{dk=0l}(\theta, r|R)|V_l(\theta, r|R)|Z_{dk=0l}(\theta, r|R)\rangle$$

$$l = 1, 2 \tag{9a}$$

and the corresponding dressed-*diabatic* coupling terms:

6363

dx.doi.org/10.1021/jp412738s | J. Phys. Chem. A 2014, 118, 6361−6366

$$\tilde{V}_{12}(R) = \langle Z_{dk=0l=1}(\theta,r|R)|V_{12}(\theta,r|R)|Z_{dk=0l=2}(\theta,r|R)\rangle \tag{9b}$$

With these matrix elements is formed the dressed-diabatic potential matrix:

$$\tilde{\mathbf{V}}(R) = \begin{pmatrix} \tilde{V}_1(R) & \tilde{V}_{12}(R) \\ \tilde{V}_{12}(R) & \tilde{V}_2(R) \end{pmatrix} \tag{10}$$

Diagonalizing this matrix, yields the two adiabatic-via-dressed-diabatic potential matrix, $u_{dl}(R)$, $l = 1, 2$.

The BO adiabatic PESs were calculated by employing the internally contracted multireference-configuration interaction (MRCI) method and the Davidson correction[40] using the MOLPRO program.[41] The calculations of the NACTs (along chosen circles) were carried out at the state-average CASSCF level using the same program. More details on both types of calculations are given in Appendix 2 of ref 9.

Figure 3 presents two $R$-dependent, dressed-adiabatic potential curves: the dressed-adiabatic potential, $u_{a0}(R)$
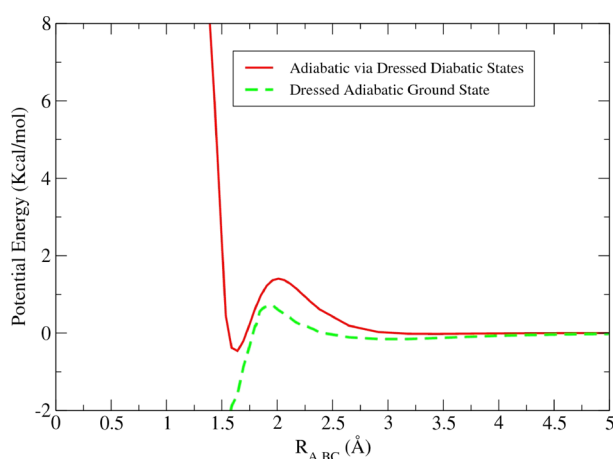


**Figure 3.** Dressed potential energy curves as calculated by employing the vib-rotational manifold. Two curves are shown: (i) dressed adiabatic potential $u_a(R)$ (see eq 8); (ii) adiabatic via dressed diabatic potential $u_d(R)$ obtained by diagonalizing the dressed *diabatic* potential matrix, $\tilde{\mathbf{V}}(R)$ (see eqs 9 and 10).

(based on the corresponding (lowest) adiabatic PES), and $u_{d1}(R)$, which is the lower eigenvalue that results from diagonalizing the corresponding dressed-diabatic potential matrix given in eq 10.

## V. ANALYSIS AND CONCLUSIONS

To analyze the results of the previous section, we somewhat extend the last statement given in the previous section: Two types of dressed-*adiabatic* PES curves are presented in Figure 3: The first is the dressed-ab initio potential that results solely from solving the electronic eigenvalue problem. The second type results from diagonalizing the 2 × 2 dressed-diabatic potential matrix calculated using the two lowest adiabatic PESs and the corresponding ADT (mixing) angles dominated by the two effects, namely the JT effect and the RT effect.

The more interesting part of our study is the comparison between the two types of *dressed-adiabatic potential curves* along the close interaction region in the vicinity of the adiabatic barrier. In contrast to our previous study based solely on the JT effect,[4] the present one shows significant differences between

the two corresponding curves in that region that are predominantly caused by the inclusion of the RT effect. Thus, indeed it is not enough to incorporate the JT effect but one has also to include the RT effect. In other words, the inclusion of the RT effect may lead to conclusions significantly different from those that were based solely on the JT effect.

Recalling the dynamical studies within the BO approximation, we remind the reader that these calculations produced a wealth of data that was compared with experiment. Encouraging agreements were obtained for all (or at least for most) *types* of measurements ranging from temperature dependent rate constants to energy dependent state-to-state differential cross sections. These facts imply, now (in contrast to what was claimed in our previous article[4]) that these results for the title system have to be eventually reproduced, again employing more relevant PESs.

We still have to be cautious for the following reason: When the multiarrangement channel Schrödinger equation is being solved, deriving **S**-matrix elements and finally the various cross sections requires more than just employing the vib-rotational manifold for forming averaged potential average surfaces as is done here.

It is our hope that the dressed-potential approach and in particular the comparison between the two types of adiabatic potential curves yield the relevant information for the importance of the topological effects in molecular exchange processes.

## ■ APPENDIX I: VIB-ROTATIONAL EIGENFUNCTIONS AND THE CORRESPONDING TRANSLATIONAL DRESSED-POTENTIAL

The Hamiltonian $H$, to be considered is given in the form

$$H(\theta,r|R) = -\frac{\hbar^2}{2\mu_r}\frac{\partial^2}{\partial r^2} + \frac{1}{2\mu_r r^2}\mathbf{j}^2 + V(\theta,r|R) \tag{I.1}$$

where $\mathbf{j}^2$ is an operator given in the form

$$\mathbf{j}^2 = -\hbar^2 \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} \tag{I.2}$$

The aim is to solve the following eigenvalue problem:

$$(H(r,\theta|R) - \varepsilon(R))Z(r,\theta|R) = 0 \tag{I.3}$$

and for this purpose $Z(r,\theta|R)$ is expanded in terms of Legendre polynomials, $P_j(\theta)$, and a set of vibrational eigenfunctions $Q_n(r|R)$, namely,

$$Z_k(r,\theta|R) = \sum_{j,n}^{N} a_{kjn}(R)\, P_j(\theta)\, Q_n(r|R) \tag{I.4}$$

where $a_{kjn}(R)$ are $R$-dependent coefficients to be determined. As for $Q_n(r|R)$ ($\equiv Q_n(r|R,\theta_0)$), $n = \{1,N\}$, they are derived from the vibrational eigenvalue problem:

$$\left(-\frac{\hbar^2}{2\mu_r}\frac{\partial^2}{\partial r^2} + V(r|R,\theta=\theta_0) - \tilde{\varepsilon}_n(R,\theta=\theta_0)\right)Q_n(r|R,\theta=\theta_0) = 0 \tag{I.5}$$

The algebraic eigenvalue problem (to calculate the $a_{knj}(R,\theta_0)$ coefficients) is based on the following matrix elements:

$$H_{njn'j'}(R,\theta_0) = \langle P_j Q_n | \Delta V(r,\theta|R,\theta_0) | Q_{n'} P_{j'} \rangle$$
$$+ \frac{\hbar^2}{2\mu_r} \langle Q_n | r^{-2} | Q_{n'} \rangle j(j+1)\delta_{jj'} + \tilde{\varepsilon}_n(R,\theta_0)\delta_{jj'}\delta_{nn'} \quad (\text{I.6})$$

Here $\tilde{\varepsilon}_n(R,\theta_0)$, $n = \{1, N\}$, are the corresponding vibrational eigenvalues, and $\Delta V(r,\theta|R,\theta_0)$ stands for the angular perturbation:

$$\Delta V(r,\theta|R,\theta_0) = V(r,\theta|R) - V(r|R,\theta_0)$$

and

$$\langle P_j Q_n | \Delta V(r,\theta|R,\theta_0) | Q_{n'} P_{j'} \rangle =$$
$$\int_{r_i}^{r_f} dr' \int_{-\pi/2}^{+\pi/2} d\theta' \, P_j(\theta') \, Q_n(r'|R,\theta_0) \, \Delta V(r',\theta'|R,\theta_0)$$
$$Q_{n'}(r'|R,\theta_0) \, P_{j'}(\theta') \quad (\text{I.7})$$

Once the matrix elements $H_{njn'j'}$ are calculated, the matrix has to be diagonalized to derive the eigenvalues $\lambda_k(R)$ and the corresponding eigenvectors, $\mathbf{a}_k(R)$. The lowest eigenfunction $Z_{k=0}(r,\theta|R)$ required for the present study is given in the form

$$Z_0(r,\theta|R,\theta_0) = \sum_{j=0n=0}^{N} a_{njk=0}(R,\theta_0) \, P_j(\theta) \, Q_n(r|R,\theta_0) \quad (\text{I.8})$$

The present study is concerned only with the lowest dressed-translational potentials as calculated for a series of $R$ values.

$$W_0(R) = \langle Z_0(r,\theta|R) | \Delta V(r,\theta|R,\theta_0) | Z_0(r,\theta|R) \rangle \quad (\text{I.9})$$

## ■ AUTHOR INFORMATION

### Corresponding Author
*M. Baer: e-mail, michaelb@fh.huji.ac.il.

### Notes
The authors declare no competing financial interest.

## ■ REFERENCES

(1) Kuppermann, A. and Abrol, R. In *The Role of Degenerate States in Chemistry*, Baer, M., Billing, G. D., Eds.; Advances in Chemistry and Physics; AIP: New York, 2002; Vol. *124*, pp 283−322.

(2) Clary, D. C. Theoretical Study of Geometric Phase Effects in the Hydrogen-Exchange Reaction. *Science* 2005, *309*, 1227−1230.

(3) Lepetit, B.; Abrol, R.; Kuppermann, A. Geometric Phase Effects in H₃ Predissociation. *Phys. Rev. A* 2007, *76*, 040702−040705.

(4) Das, A.; Sahoo, T.; Mukhopadhyay, D.; Adhikari, S.; Baer, M. Dressed Adiabatic and Diabatic Potentials to Study Conical Intersections for F+H₂. *J. Chem. Phys.* 2012, *136*, 054104−1−054104−6.

(5) Baer, R.; Charutz, D. M.; Kosloff, R.; Baer, M. A Study of Conical Intersection Effects on Scattering Processes: The Validity of Adiabatic Single Surface Approximations within an Quasi-Jahn-Teller Model. *J. Chem. Phys.* 1996, *105*, 9141−9152.

(6) Charutz, D. M.; Baer, R.; Baer, M. A Study of Degenerate Vibronic Coupling Effects on Scattering Processes: Are Resonances Affected by Degenerate Vibronic Coupling? *Chem. Phys. Lett.* 1997, *265*, 629−637.

(7) Adhikari, S.; Billing, G. D. The Conical Intersection Effects and Adiabatic Single-Surface Approximations on Scattering Processes: A Time-Dependent Wave Packet Approach. *J. Chem. Phys.* 1999, *111*, 40−47.

(8) Csehi, A.; Bende, A.; Halász, G. J.; Vibók, Á.; Das, A.; Mukhopadhyay, D.; Mukherjee, S.; Adhikari, S.; Baer, M. Dressed Adiabatic and Diabatic Potentials for the Renner-Teller/Jahn-Teller F + H₂ System. *J. Phys. Chem. A* 2013, *117*, 8497−8505.

(9) Csehi, A.; Bende, A.; Halász, G. J.; Vibók, Á.; Das, A.; Mukhopadhyay, D.; Baer, M. A Tri-Atomic Renner-Teller System Entangled with Jahn-Teller Conical Intersections. *J. Chem. Phys.* 2013, *138*, 024113−1−024113−10.

(10) Stark, K.; Werner, H.-J. An Accurate Multireference Configuration Interaction Calculation of the Potential Energy Surface for the F+H₂→HF+H Reaction. *J. Chem. Phys.* 1996, *104*, 6515−6530.

(11) Das, A.; Mukhopadhyay, D.; Adhikari, S.; Baer, M. Diabatization of the Reactive F+H2 System Employing Rigorous Berry Phases. *Eur. Phys. J. D* 2011, *65*, 373−381.

(12) Das, A.; Mukhopadhyay, D. Jahn−Teller Intersections Involving Excited States of the F+H₂ System: Identification and Influence on the Reaction System. *Chem. Phys.* 2013, *412*, 51−57.

(13) Baer, M. Adiabatic and Diabatic Representations for Atom-Molecule Collisions: Treatment of the Collinear Arrangement. *Chem. Phys. Lett.* 1975, *35*, 112−118.

(14) Baer, M. On the Existence of Diabatic Potentials and the Quantization of the Non-Adiabatic Matrix. *J. Phys. Chem. A* 2000, *104*, 3181−3184.

(15) Baer, M.; Lin, S. H.; Alijah, A.; Adhikari, S.; Billing, G. D. The Extended Approximated Born-Oppenheimer Equation I. *Phys. Rev. A* 2000, *62*, 032506−032513.

(16) Lipoff, S. H.; Herschbach, D. Low-Energy Limit for Tunnelling Subject to an Eckart Potential Barrier. *Mol. Phys.* 2010, *108*, 1133−1143.

(17) Herschbach, D. Molecular Collisions, from Warm to Ultracold. *Faraday Discuss.* 2009, *142*, 9−23.

(18) It is important to emphasize that Lipoff and Herschbach did not propose this particular comparison but made the following suggestion: "Curiously although F+H₂ (Dressed) adiabatic potentials were evaluated[33] no use was made of them to examine the entrance channel collision dynamics. In the future it *should become standard and blessed practice* to consider the Dressed potentials in discussion of any ultra-cold reaction."[19]

(19) Reference 33 mentioned in this paragraph is ref 20 of the present list (see below).

(20) Rosenman, E.; Hochman-Kowal, Z.; Persky, A.; Baer, M. A Three Dimensional Quantum Mechanical Study of the F+H₂/D₂ Reactions on a New Potential Energy Surface. *Chem. Phys. Lett.* 1996, *257*, 421−428.

(21) Gilibert, M.; Baer, M. Quantum Mechanical Theory of Reactive Collisions via Electronic Non-Adiabatic Transitions. The Three Dimensional F(²P₁/₂, ²P₃/₂)+H₂ System as a Test Case. *J. Phys. Chem.* 1995, *99*, 15748−15757.

(22) Alexander, M. H.; Manolopoulos, D. E.; Werner, H.-J. An Investigation of the F+H₂ Reaction Based on a Full Ab Initio Description of the Open-Shell Character of the F(²P) Atom. *J. Chem. Phys.* 2000, *113*, 11084−11100.

(23) Born, M.; Oppenheimer, J. R. On the Quantum Theory of Molecules. *Ann. Phys.(Leipzig)* 1927, *84*, 457−488.

(24) Born, M. *Festschrift Goett. Nach. Math. Phys.* 1951, *K1*, 1.

(25) Born, M. and Huang, K. *Dynamical Theory of Crystal Lattices*; Oxford University: New York, 1954; Chapter IV.

(26) Top, Z. H.; Baer, M. Incorporation of Electronically Nonadiabatic Effects into Bimolecular Reactive Systems. I. Theory. *J. Chem. Phys.* 1977, *66*, 1363−1371.

(27) Alijah, A.; Baer, M. The Electronic Adiabatic-Diabatic Transformation Matrix: A Theoretical and Numerical Study of a Three-State System. *J. Phys. Chem. A* 2000, *104*, 389−396.

(28) Vértesi, T.; Bene, E.; Vibók, Á.; Halász, G. J.; Baer, M. The N-State Adiabatic-to-Diabatic Transformation Angle: Theory and Application. *J. Phys. Chem. A* **2005**, *109*, 3476−3484.

(29) Sarkar, B.; Adhikari, S. Extended Born-Oppenheimer Equation for a Three-State System. *J. Chem. Phys.* **2006**, *124*, 074101−1−074101−18.

(30) Sarkar, B.; Adhikari, S. Curl Condition for a Four-State Born-Oppenheimer System Employing the Mathieu Equation. *J. Phys. Chem. A* **2008**, *112*, 9868−9885.

(31) Das, A.; Mukhopadhyay, D.; Adhikari, S.; Baer, M. Renner−Teller Intersections along the Collinear Axes of Polyatomic Molecules: $H_2CN$ as a Case Study. *J. Chem. Phys.* **2010**, *133*, 084107−1−084107−11.

(32) Das, A.; Mukhopadhyay, D. Jahn-Teller Intersections Induced by Introduction of Bending in Linear Polyatomics: Study with HCNH, a Selected Molecular System. *J. Phys. Chem. A* **2012**, *116*, 1774−1885.

(33) Das, A.; Mukhopadhyay, D. Study of Nonadiabatic Effects in Low-Lying Electronic States of HCNH with Implication in its Dissociation to HCN and HNC. *J. Phys. Chem. A* **2013**, *117*, 8680−8690.

(34) Baer, M. *Beyond Born Oppenheimer; Electronic non-Adiabatic Coupling Terms and Conical Intersections*; Wiley & Sons Inc: Hoboken, NJ, 2006; (a) Chapter 5.5, (b) Section 8.3.3.

(35) Top, Z. H.; Baer, M. Incorporation of Electronic Nonadiabatic Effects into Bimolecular Reactive Systems. The Collinear ($H_2 + H^+$, $H_2^+ + H$) System. *Chem. Phys.* **1977**, *25*, 1−18 (see Appendix A).

(36) Levy, C.; Halász, G. J.; Vibók, Á.; Bar, I.; Zeiri, Y.; Kosloff, R.; Baer, M. A Novel Intraline of Conical intersections for Methylamine: A Theoretical Study. *Int. J. Quantum Chem.* **2009**, *109*, 2482−2489.

(37) Top, Z. H.; Baer, M. Incorporation of Electronic Nonadiabatic Effects into Bimolecular Reactive Systems. The Collinear ($H_2 + H^+$, $H_2^+ + H$) System. *Chem. Phys.* **1977**, *25*, 1−18.

(38) Baer, M.; Niedner, G.; Toennies, J. P. A Three-Dimensional Quantum Mechanical Study of Vibrationally Resolved Charge Transfer Processes in $H^+ + H_2$ at $E_{cm}$=20 eV. *J. Chem. Phys.* **1989**, *91*, 4169−4182.

(39) Liao, C. L.; Xu, R.; Flesh, G. D.; Baer, M.; Ng, C. Y. Experimental and Theoretical Total State-Selected and State-to-State Absolute Cross Sections. I. The $H_2+(X,v')$ + Ar Reaction. *J. Chem. Phys.* **1990**, *93*, 4818−4831.

(40) Langhoff, S. R.; Davidson, E. R. Configuration Interaction Calculations on the Nitrogen Molecule. *Int. J. Quantum Chem.* **1974**, *8*, 61−72.

(41) MOLPRO is a package of ab initio programs written by H.-J. Werner and P. J. Knowles with contributions from J. Almlöf et al.