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Citation: *The Journal of Chemical Physics* **136**, 054104 (2012); doi: 10.1063/1.3679406

View online: <http://dx.doi.org/10.1063/1.3679406>

View Table of Contents: <http://aip.scitation.org/toc/jcp/136/5>

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Dressed adiabatic and diabatic potentials to study conical intersections for F + H₂

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(Received 28 November 2011; accepted 6 January 2012; published online 2 February 2012)

We follow a suggestion by Lipoff and Herschbach [Mol. Phys. **108**, 1133 (2010)] and compare *dressed* and *bare* adiabatic potentials to get insight regarding the low-energy dynamics (e.g., *cold reaction*) taking place in molecular systems. In this particular case, we are interested to study the effect of conical intersections (*ci*) on the interacting atoms. For this purpose, we consider *vibrational dressed adiabatic* and *vibrational dressed diabatic* potentials in the entrance channel of reactive systems. According to our study, the most one should expect, in case of F + H₂, is a mild effect of the (1, 2) *ci* on its reactive/exchange process—an outcome also supported by experiment. This happens although the corresponding *dressed* and *bare* potential barriers (and the corresponding van der Waals potential wells) differ significantly from each other. © 2012 American Institute of Physics. [doi:10.1063/1.3679406]

I. INTRODUCTION

Recently, we published several articles concerning the *diabatic* potential energy surfaces (PES) of the F + H₂ (Ref. 1) within the Born-Oppenheimer (BO) treatment.² Such studies require deriving *ab initio* adiabatic PESs as well as *ab initio* non-adiabatic coupling terms (NACTs) and forming adiabatic-to-diabatic transformation (ADT) angles (mixing angles)^{3,4} with integer Berry phases along closed contours⁵⁻⁷ (to guarantee single-valued diabatic potentials). In these articles, procedures of how to carry out these calculations in the most efficient and reliable way were examined.

The main reason for the present study is not so much to deliver a more up-to-date PES for the title reaction but to find out to what extent the *cis* of this system affect the lowest adiabatic PES. To clarify what we have in mind, we refer to a recent important article by Lipoff and Herschbach (LH) [Ref. 8(a)] in which they distinguish between *bare* and *dressed* potentials (while referring to the reactive F + H₂ system). Following this presentation, the *bare* PES is the one obtained from the electronic structure calculations (in other words, the BO lowest adiabatic PES) and the *dressed* PES is the effective potential felt by the reactants when approaching each other at (very) low temperatures (as encountered, e.g., in *cold reactions*⁹). While doing this comparison LH showed that the *dressed* potential barrier and the van der Waals potential well (both in the entrance channel) differ significantly from the corresponding *bare* magnitudes.

LH *summarized* the discussion on this subject with the following statements:

“Curiously although F + H₂ (*dressed*) adiabatic potentials were evaluated,^{3,3} 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.”^{10,11}

Here, we follow this suggestion and consider two types of *dressed* potentials: one as formed by the lowest BO *adiabatic* PES and the second as formed by the two lowest *diabatic* potentials as will be described below. It is our hope that this comparison will shed light on the role of the above mentioned *ci* in the entrance arrangement.

Our study is extended (as compared with the LH study) in the following way. The comparisons between the various potentials will not be done for the full three-dimensional potential but for two-dimensional potentials as calculated for frozen vibrational coordinates *r* and the integration is, consequently, carried out for the *rotational* basis sets only. This kind of treatment is expected to enhance the *transparency* of the comparison. In a subsequent publication, the comparisons will also include the full three-dimensional *dressed* potentials as suggested by LH.

Two comments have to be made:

- (i) We remind the reader that diabatic potentials were already calculated for this system long time ago,¹² but these were derived in a very approximate way ignoring the relevant BO-NACTs.
- (ii) In the present study, just like in our recent studies,¹ we do not include the spin-orbit coupling (such calculations were reported, e.g., in Refs. 13 and 14). It is very likely

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that as long as this coupling is ignored the corresponding *dynamic* calculations are not trustful, but our main concern at this stage is the BO adiabatic and diabatic potentials and not the dynamic calculations.

II. BACKGROUND

In our previous publications, we discussed two approaches to form diabatic potentials; both are based on deriving ADT angles from BO-NACTs. In Refs. 1(a) and 1(b), the ADT angles were based on one NACT, $\tau_{12}(\mathbf{R}, \theta|r)$, which couples the two lower adiabatic states, i.e., a Σ -state and one of the Π -states. In Ref. 1(c), the ADT angles were based on two NACTs, namely, the previously mentioned $\tau_{12}(\mathbf{R}, \theta|r)$ and $\tau_{23}(\mathbf{R}, \theta|r)$, which is formed by two (upper) Π -states. In the present study, we consider the two-state ADT angles based on the first approach.

The details how these ADT angles, $\gamma(\mathbf{R}, \theta|r)$, are calculated for the title system are given in the two Refs. 1(a) and 1(b) (see, also, Appendix). Here, we just mention that these calculations are based on line integrals of the kind^{3,4}

$$\gamma_{12}(\varphi, q|r) = \int_0^\varphi \tau_{\varphi 12}(\varphi', q|r) d\varphi', \quad (1)$$

(carried out along open and closed circular contours) where $\tau_\varphi(\varphi, q|r)/q$ is the corresponding *angular* component of the NACT, $\tau_{12}(\varphi, q|r)$, with the operator τ_φ defined as $\tau_\varphi(\varphi, q|r) = \langle \chi_1(\varphi, q|r) | (\partial/\partial\varphi) \chi_2(\varphi, q|r) \rangle$. The two functions $\chi_j(\varphi, q|r)$; $j = 1, 2$ are the eigenfunctions related to the two lower states, mentioned earlier, and q and φ are the relevant polar coordinates with regard to some point on a plane (see Fig. 1). In other words the points along the circular contour, Γ , are now described in terms of polar coordinates (q, φ) . The two systems of coordinates, (q, φ) and (\mathbf{R}, θ) , for a given r -value, are connected via simple geometrical relations (see Fig. 1).

Given the two adiabatic PESs $u_j(\varphi, q|r)$; $j = 1, 2$, the corresponding diabatic potentials $V_1(\varphi, q|r)$, $V_2(\varphi, q|r)$, and

$V_{12}(\varphi, q|r)$, are derived from the following set of equations:¹⁵

$$\begin{aligned} V_1(\varphi) &= u_1(\varphi) \cos^2 \gamma(\varphi) + u_2(\varphi) \sin^2 \gamma(\varphi), \\ V_2(\varphi) &= u_1(\varphi) \sin^2 \gamma(\varphi) + u_2(\varphi) \cos^2 \gamma(\varphi), \\ V_{12}(\varphi) &= (1/2) \{u_2(\varphi) - u_1(\varphi)\} \sin(2\gamma(\varphi)), \end{aligned} \quad (2)$$

where $\gamma(\varphi)$ stands for $\gamma(\varphi, q|r)$ and is given in Eq. (1). The transformation that yields the diabatic potentials is presented explicitly to show that in order to guarantee the single-valuedness of these potentials the angle γ , once calculated along a closed circle, has to be equal to $n\pi$, where n is an integer.^{1,6,7} This difficulty is not always easy to surmount, in particular when the radii, q , of the circles (see Fig. 1) become large. Recently, this difficulty was treated via a novel approach based on *complementary* line integrals^{1(a),1(b)} (see Appendix).

As mentioned earlier, the LH suggestion will be applied here for two-dimensional configuration spaces, formed by keeping fixed, the vibrational coordinate r . The single-state dressed adiabatic potential, $u_s(\mathbf{R}|r)$, is calculated employing the expression

$$u_s(\mathbf{R}|r) = \langle \zeta_1(\theta|\mathbf{R}, r) | u_{a1}(\theta|\mathbf{R}, r) | \zeta_1(\theta|\mathbf{R}, r) \rangle, \quad (3)$$

where $u_{a1}(\theta|\mathbf{R}, r)$ is the *bare* Stark-Werner (SW) potential and $\zeta_1(\theta|\mathbf{R}, r)$ is the corresponding *rotational* eigenfunction of $u_{a1}(\theta|\mathbf{R}, r)$. The double-state lowest dressed adiabatic potential, $u_d(\mathbf{R}|r)$, is obtained by diagonalizing the dressed *diabatic* potential matrix, $\mathbf{V}(\mathbf{R}|r)$, given in the form

$$\mathbf{V}(\mathbf{R}|r) = \begin{pmatrix} \tilde{V}_1(\mathbf{R}|r) & \tilde{V}_{12}(\mathbf{R}|r) \\ \tilde{V}_{12}(\mathbf{R}|r) & \tilde{V}_2(\mathbf{R}|r) \end{pmatrix}, \quad (4)$$

where $\tilde{V}_j(\mathbf{R}|r)$; $j = 1, 2$ and $\tilde{V}_{12}(\mathbf{R}|r)$ are calculated employing the following expressions:

$$\tilde{V}_j(\mathbf{R}|r) = \langle \xi_j(\theta|\mathbf{R}, r) | V_j(\theta|\mathbf{R}, r) | \xi_j(\theta|\mathbf{R}, r) \rangle, \quad (5a)$$

$$\tilde{V}_{12}(\mathbf{R}|r) = \langle \xi_1(\theta|\mathbf{R}, r) | V_{12}(\theta|\mathbf{R}, r) | \xi_2(\theta|\mathbf{R}, r) \rangle. \quad (5b)$$

Here, $\xi_j(\theta|\mathbf{R}, r)$; $j = 1, 2$ are the corresponding *rotational* (diabatic) eigenfunctions of the two corresponding diabatic potentials $V_j(\theta|\mathbf{R}, r)$; $j = 1, 2$.

In the numerical study, we concentrate on the two *dressed* potentials, $u_s(\mathbf{R}|r)$ and $u_d(\mathbf{R}|r)$.

III. NUMERICAL RESULTS

Whereas the calculations of the adiabatic potentials are straightforward, the calculations of the diabatic ones (in particular along angular intervals at the vicinity of $\theta \sim \pi/2$) are more involved and therefore have to be carried out with some care. The details will be given in our next, more extended, publication. At this stage we mention that these calculations, in contrast to the earlier ones,¹ are now done for the full angular interval $0 \leq \theta \leq \pi$. The translational interval is also increased to become, $3.0 \leq R \leq 10.0$ a.u.

In what follows are discussed PESs and the corresponding potential energy curves relevant for the present study. These are based on the SW pure adiabatic PESs (Ref. 12) calculated by employing the internally contracted Multi Reference Configuration Interaction (MRCI) method and the

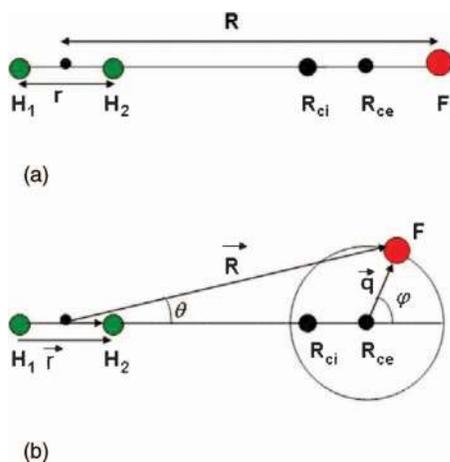


FIG. 1. A schematic picture of the system of coordinates: (a) The point of (1, 2) *ci* (at R_{ci}), the center of all circular contours (at R_{ce}), and positions of the three atoms along the collinear axis. (b) Two cartesian systems of coordinates: $(\mathbf{R}, \theta|r)$ vs. $(\varphi, q|r)$.

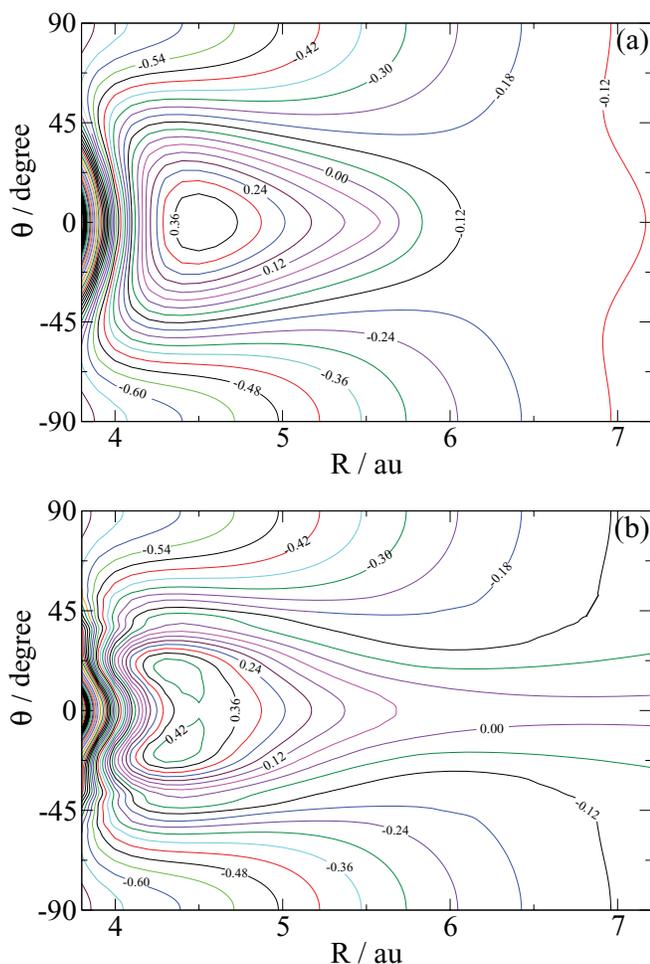


FIG. 2. Equi-potential lines of the two lower potentials, namely, $u_{a1}(R, \theta)$ and $V_1(R, \theta)$, emphasizing the differences of their barrier structure (see text). In (a) is presented the *adiabatic* potential, $u_{a1}(R, \theta)$ and in (b) is presented the *diabatic* potential, $V_1(R, \theta)$. The calculations were carried out for a plane formed by a fixed vibrational coordinate $r (=r_{HH}) = 1.8$ a.u.. Contours are drawn in steps of 0.06 kcal/mol.

Davidson correction^{16(a)} using the MOLPRO program.^{16(b)} More details are given in Ref. 1.

In Fig. 2 are given two panels (a) and (b) presenting the equi-potential lines for the two lower respective vibronic potentials, $u_{a1}(R, \theta)$ and $V_1(R, \theta)$, as calculated for $r (=r_{HH}) = 1.8$ a.u. (similar equi-potential lines for $r = 1.6$ a.u. and $r = 1.4$ a.u., are presented in Refs. 1(a) and 1(b), respectively). It is well seen that the two potentials differ significantly from each other: Whereas the adiabatic potential, $u_{a1}(R, \theta)$, is characterized by a single (mild) peak, which occurs at a point on the collinear axis at $R \sim 4.5$ a.u., the diabatic potential, $V_1(R, \theta)$, possesses two symmetric peaks at $(R, \theta) \cong (4.35$ a.u., $\pm 20^\circ)$ and a typical saddle structure with the minimum/maximum point located on the collinear axis at $R \sim 4.5$ a.u.

In Fig. 3, three panels (a), (b), and (c) presenting in each case three R-dependent, adiabatic, vibrational potential curves are given: the two *dressed* potentials, $u_s(R|r)$ and $u_d(R|r)$, and the corresponding *bare* potential $u_{a1}(\theta = 0, R|r)$. The curves in each panel are characterized by two important features; (a) The bare potentials differ significantly from the

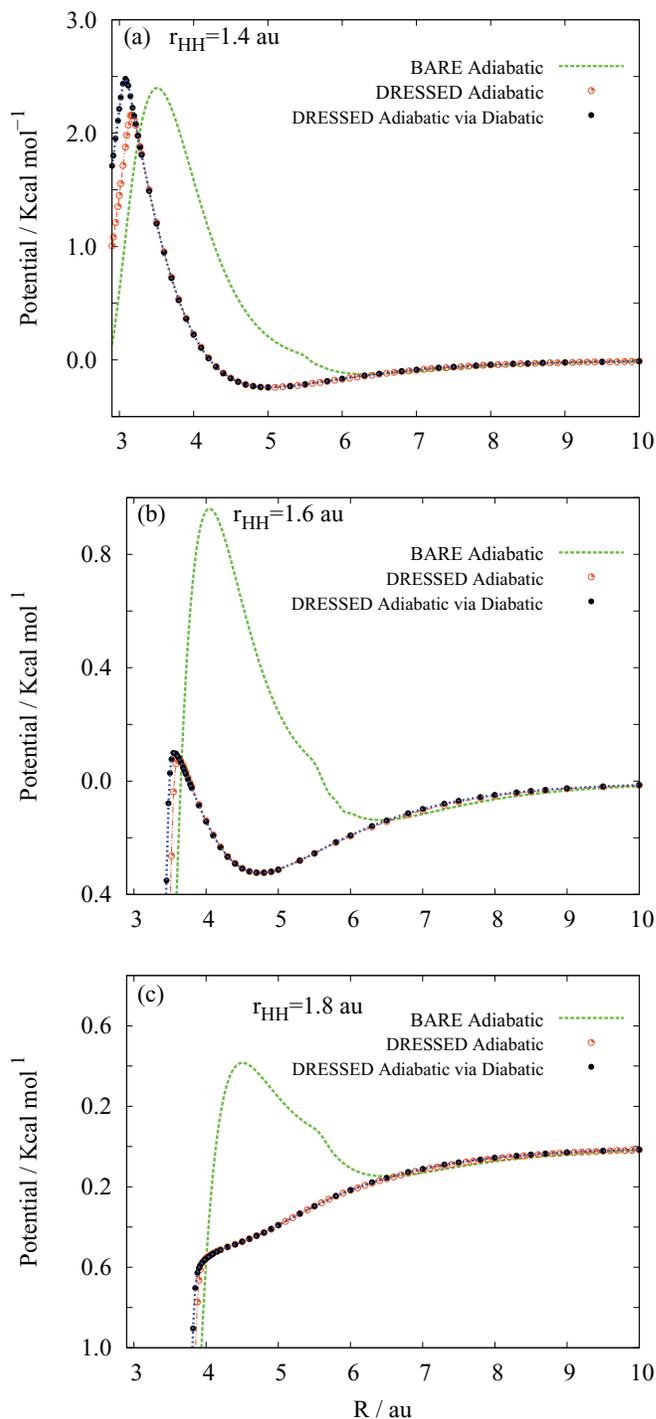


FIG. 3. Potential curves as calculated for fixed vibrational coordinates $r (=r_{HH})$. In each panel are presented three curves: (i) The bare adiabatic potential $u_{a1}(R, \theta|r)$ calculated at $\theta = 0$; (ii) The vibronic dressed potential $u_s(R|r)$ (see Eq. (3)); (iii) The vibronic dressed potential $u_d(R|r)$ obtained by diagonalizing the dressed *diabatic* potential matrix, $V(R|r)$ (see Eqs. (4) and (5)). The results for $r_{HH} = 1.4, 1.6,$ and 1.8 a.u. are shown in panels (a), (b), and (c), respectively.

dressed ones and (b) the two dressed potentials, for all practical purposes, overlap each other.

IV. ANALYSIS AND CONCLUSIONS

The large deviation of the bare potential from the dressed one was already elaborated by LH when they compared

the three-dimensional dressed potential with the collinear bare potential. They found the barrier of the *dressed* potential to be much narrower and significantly lower (see also Ref. 11) as compared to the *bare* potential. In the present study where *several* vibronic bare and dressed potentials are compared, various kinds of differences become apparent. Thus, in case of $r = 1.4$ a.u. the two kinds are of similar heights, but the dressed potential is much narrower, in case of $r = 1.6$ a.u. the dressed potential is significantly lower and as before much narrower, and in case of $r = 1.8$ a.u. the structure of the two potential curves is altogether different: whereas the dressed potential is a smooth increasing function of R (thus without a barrier), the bare potential has a barrier but which is lower and much broader as compared to the previous ones.

The more interesting result of our study is the nice fit between the two dressed potentials for all three vibronic cases. Mathematically speaking, these two types of curves are not expected to overlap, but if they do it will happen only under restrictive conditions. From the physical point of view, this overlap indicates that the $(1,2)ci$, although it exists, does not affect significantly the lowest adiabatic potential. In other words, dynamic calculations employing only the lowest adiabatic surface, as are done within the BO approximation,² are expected to be only slightly affected by more extensive multi-state treatments.

Recalling the dynamical studies within the BO approximation,^{11,17–20} we remind the reader that these and many other 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 that the title system can be studied reliably well within the BO *approximation* although its potentials are probably affected, at certain regions, by the $(1,2)ci$. It seems that the conclusion of the present study supports this finding. Still we have to be cautious about this statement for two reasons: (i) It could be that the effect of the ci is not sensitive to the rotational motion of the particles; (ii) We have to remember that solving the relevant multi-state Schrödinger equation, in particular, for (ultra) *cold reactions* requires more than just employing vibronic potentials as analyzed here.

As a final subject, we return to an issue related to the BO treatment to yield reliable diabatic potentials. Two points are of concern:

- There is no doubt that theories based on the BO-NACTs (as opposed to other kinds¹²) are, currently, the more trustful ones to yield the required diabatic potentials for molecular systems (see, for instance, a sample of references given in the present article^{5(c),21–47}).
- Among these is also listed the *line integral* approach,^{3,4,6} which is based on line integrals along closed contours to form ADT angles (see Eq. (1)) and, accordingly, diabatic potentials (see Eq. (2)). It is true that this approach is criticized sporadically for not delivering *strictly* diabatic potentials (see, e.g., Ref. 48(a) and a rebuttal in Ref. 48(b)), but then it was

tested for numerous cases along the last thirty years and was found to be trustful (utilizing, when necessary, extensions^{1(a),1(b),7}) for forming *approximate* diabatic potentials (see, for instance, a sample of references: Refs. 5(c), 21(c), 21(d), 22, 23, 29–33, 35–37, 39–41, 43, and 44). In the Appendix is discussed the extension used in the present study.

ACKNOWLEDGMENTS

A.D. acknowledges CSIR, India for research fellowship. D.M and S.A. acknowledge the BRNS, India for grants (Sanction No. 2009/37/42/BRNS) in computational facilities.

APPENDIX: DERIVATION OF THE COMPLEMENTARY LINE INTEGRAL

As mentioned in the article, we find that for the larger (circular) contours ($q \geq 3$ a.u., in our case) the line integral (in Eq. (1)) does not yield the expected phase, namely, $n\pi$ (see Fig. 4). In such a situation, we used to solve the line integrals for several states.⁷ In our present case, we developed a new methodology for this purpose based on two states.

This treatment is based on the fact that the hydrogen-hydrogen-fluorine (HHF) system is *symmetric* with respect to the collinear axis (see Fig. 1). Consequently, for any circular contour with its center located on the collinear axis, we get that $\gamma_{12}(\varphi = 2\pi|q) = 2\gamma_{12}(\varphi = \pi|q)$. However, since we demand that for a full circle $\gamma_{12}(\varphi = 2\pi|q) = \pi$, we should get for half a circle, $\{0, \pi\}$: $\gamma_{12}(\varphi = \pi|q) = \pi/2$. Having established this result, the idea is to carry out the line integral in Eq. (1) twice – each time with a different initial point:

- Integrating forward (the ordinary way), starting at $\varphi = 0$ and ending at some intermediate value $\varphi = \varphi_{\text{fin}}$ (see Fig. 5) thus yielding $\gamma_{12}(\varphi|q) = \gamma_{12}^{(f)}(\varphi|q)$ along the interval $0 \leq \varphi \leq \varphi_{\text{fin}}$. Here “f” stands for *forward*.

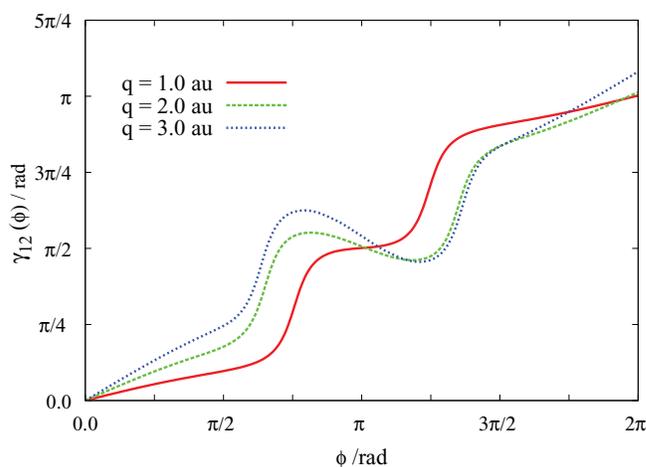


FIG. 4. Adiabatic-to-diabatic-transformation (mixing) angle, $\gamma_{12}(\varphi|q)$, for circular contours at $R = R_{ce} = 6$ a.u. along the interval $0 \leq \varphi \leq 2\pi$ as calculated employing Eq. (1).

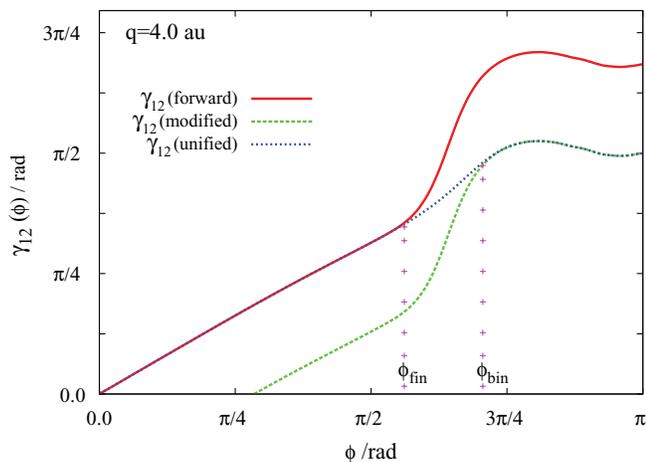


FIG. 5. Adiabatic-to-diabatic-transformation (mixing) angle, $\gamma_{12}(\phi|q)$ at $R = R_{ce} = 6$ a.u., for circular contours ($q = 4$ a.u.) along the interval $0 \leq \phi \leq \pi$: the first curve, $\gamma_{12}^{(f)}(\phi|q)$, (—) is calculated employing Eq. (1) in the forward direction; the second curve, $\gamma_{12}^{(m)}(\phi|q)$, (-----) is calculated employing Eq. (1) in the backward direction (thus forming $\gamma_{12}^{(b)}(\phi|q)$), and then, further, employing Eq. (A1) to form the modified curve; the third curve (.....)—the unified curve—is formed by merging $\gamma_{12}^{(f)}(\phi|q)$ and $\gamma_{12}^{(m)}(\phi|q)$, and interpolating along the intermediate interval $[\phi_{fin} \leq \phi \leq \phi_{bin}]$ employing a least-squares technique.

(b) Integrating backward, namely, starting at $\phi = \pi$ and ending at $\phi = \phi_{bin}$ thus yielding $\gamma_{12}^{(b)}(\phi|q)$ for the interval $\phi_{bin} \leq \phi \leq \pi$. Here “b” stands for *backward*.

It can be shown that having $\gamma_{12}^{(b)}(\phi|q)$, we are able to form the modified part of the (ill-conditioned) $\gamma_{12}(\phi|q)$ (along the interval $\phi_{bin} \leq \phi \leq \pi$), by making the simple connection

$$\gamma_{12}^{(m)}(\phi|q) = \pi/2 - \gamma_{12}^{(b)}(\phi|q). \quad (\text{A1})$$

Here “m” stands for *modified* (see Fig. 5).

According to the procedure just described, $\gamma_{12}^{(f)}(\phi|q)$ is expected to be accurate for the lower ϕ -interval, namely, in the vicinity of $\phi \sim 0$ and up to some value $\phi = \phi_{fin}$, whereas $\gamma_{12}^{(m)}(\phi|q)$ is expected to be accurate for the upper ϕ -interval in the vicinity of $\phi \sim \pi$ and down to some value $\phi = \phi_{bin}$ (see Fig. 5). To get the full (physical) curve $\gamma_{12}^{(u)}(\phi|q)$ —where u stands for “unified”—for the interval of interest, $0 \leq \phi \leq \pi$, we *interpolate* along the intermediate region $\phi_{fin} \leq \phi \leq \phi_{bin}$ so that the two curves, $\gamma_{12}^{(f)}(\phi|q)$ and $\gamma_{12}^{(m)}(\phi|q)$, from left and right, respectively, merge *smoothly* to form one single curve. This single curve (in Fig. 5) is formed by applying the least-squares method which is based on the given values of $\gamma_{12}^{(f)}(\phi|q)$ and $\gamma_{12}^{(m)}(\phi|q)$ along the corresponding intervals: $0 \leq \phi \leq \phi_{fin}$ and $\phi_{bin} \leq \phi \leq \pi$.

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