

Diabatic states in the avoided crossing region

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Abstract. A method of performing diabatic transformation on a pair of adiabatic states in the region of sharp avoided crossings is discussed. By choosing a region $[R_1, R_2]$ where the diabatic transformation is to be made, the diabatic wavefunctions in the interval $[R_1, R_2]$ are constructed as R -dependent linear combinations of adiabatic wavefunctions at R_1 and R_2 . The method is applied to treat the adiabatic potential curves of helium calculated in hyperspherical coordinates. It is shown that the resulting coupling terms between the diabatic states are small and that the diabatic wavefunctions evolve smoothly with the hyper-radius. The limitation of this approach is also discussed.

1. Introduction

The adiabatic approximation is a widely used approach in the study of many quantum mechanical systems. If a single coordinate R can be treated as a slow variable in comparison with other coordinates r , in the adiabatic approximation one separates the Hamiltonian of the whole system in the form

$$H = -\frac{1}{2\mu} \frac{d^2}{dR^2} + H_0(R; r) \quad (1)$$

where the first term is the kinetic energy of the slow variable and $H_0(R; r)$ is the Hamiltonian of the system with a fixed R . In this approximation, the total wavefunction is expanded as

$$\Psi(R, r) = \sum_{\mu} F_{\mu}(R) \psi_{\mu}(R; r) \quad (2)$$

where the adiabatic wavefunctions are the eigensolutions of H_0 at a fixed R ,

$$H_0(R; r) \psi_{\mu}(R; r) = U_{\mu}(R) \psi_{\mu}(R; r) \quad (3)$$

and the 'radial' functions $F_{\mu}(R)$ satisfy the coupled equations

$$\left(-\frac{d^2}{dR^2} + U_{\mu}(R) - W_{\mu\mu} + 2E \right) F_{\mu}(R) + \sum_{\nu} W_{\mu\nu}(R) F_{\nu}(R) = 0. \quad (4)$$

Note that

$$\begin{aligned} W_{\mu\nu} &= 2\langle \psi_{\mu} | d/dR | \psi_{\nu} \rangle d/dR + \langle \psi_{\mu} | d^2/dR^2 | \psi_{\nu} \rangle \\ &= 2P_{\mu\nu} d/dR + Q_{\mu\nu} \end{aligned} \quad (5)$$

where the bracket indicates integration over the coordinates r . The first term $P_{\mu\nu}$ involves first-order derivatives, and the second term $Q_{\mu\nu}$ involves second-order derivatives, of the adiabatic wavefunctions with respect to R . Small values of $P_{\mu\nu}$ and $Q_{\mu\nu}$ give a measure of the 'adiabaticity' of the adiabatic wavefunctions. For the diagonal $W_{\mu\mu}$ terms only the second-order derivatives are non-zero. If one assumes that the adiabatic basis set in (2) is complete, then we have the identity

$$Q_{\mu\nu} = (P^2)_{\mu\nu} + dP_{\mu\nu}/dR. \quad (6)$$

The adiabatic approach is useful in situations where the non-adiabatic couplings between different channels μ are small. For any quantal systems, (3) and (5) provide the well defined procedure for calculating the potential curves $U_\mu(R)$ and the coupling terms $P_{\mu\nu}$ and $Q_{\mu\nu}$, respectively. The coupling among the channels can be accounted for by solving the coupled equations (4).

The above adiabatic procedure is quite straightforward, but in actual numerical applications one often does not solve (4) directly. In general the family of potential curves calculated in the adiabatic approximation show numerous localized avoided crossings. At such crossings the non-adiabatic coupling terms $P_{\mu\nu}(R)$ and $Q_{\mu\nu}(R)$ are quite large and vary rapidly with R . The strong R -dependence of the coupling terms not only makes the numerical calculation of these matrix elements cumbersome because the adiabatic wavefunctions have to be calculated over fine-meshed points, but also presents difficulty in the numerical integration of the coupled equations (4).

Various methods have been suggested in the literature (Heil *et al* 1981, Garrett and Truhlar 1981, Smith 1969, Delos and Thorson 1978) where sharp avoided crossings in the adiabatic representation can be transformed away. The general procedure is to employ a unitary matrix $C(R)$ which transforms the set of radial functions $F^a(R)$ in the adiabatic representation to a set $F^d(R)$ in the diabatic representation

$$F^d(R) = C(R)F^a(R) \quad (7)$$

where

$$dC/dR + PC = 0. \quad (8)$$

In (6), $(P)_{\mu\nu} = P_{\mu\nu}$. For the two-channel problem, one can show that

$$C(R) = \begin{pmatrix} \cos \xi(R) & \sin \xi(R) \\ -\sin \xi(R) & \cos \xi(R) \end{pmatrix} \quad (9)$$

where

$$\xi(R) = \int_R^\infty P_{12}(R') dR'. \quad (10)$$

Thus such a diabatic transformation requires the knowledge of $P_{\mu\nu}(R)$ over the whole range of R . If only a *finite* number of channels are included, the $P_{\mu\nu}$ -type coupling terms vanish between all the resulting diabatic states and thus the states are 'truly' diabatic (Smith 1969) despite that the wavefunctions are still R -dependent. In this diabatic representation, the $Q_{\mu\nu}$ -type matrix elements in general do not vanish but they are neglected in the literature. We mention that if this diabatic procedure is applied to the whole Hilbert space the diabatic wavefunctions will have no R -dependence and then all the $Q_{\mu\nu}$ terms vanish as well, see Gabriel and Taulbjerg (1974).

The above diabatic transformation procedure has been used by practitioners in atomic collisions (see for example, Kimura and Lane 1990). However, it has three

undesirable features. (i) The transformation has to be applied to all values of R instead of only in the region of avoided crossings. The resulting diabatic potential curves often deviate substantially from the original adiabatic curves even in the region where there is no obvious avoided crossing and that the off-diagonal potential coupling terms between the diabatic states are large (Heil *et al* 1981, Tan and Lin 1988). (ii) The solution of (8) or (10) requires the knowledge of P_{12} over the whole range of R , especially one needs to know this term in the asymptotic region. In the perturbed stationary state (pss) approximation for atomic collisions, it is known that there exist spurious coupling terms in this region such that the evaluation of (10) becomes inaccurate. (iii) Since $P_{\mu\nu}$ is used in calculating the rotation matrix, adiabatic wavefunctions have to be computed over very fine mesh points in the region of avoided crossing.

In this paper, our goal is to show a procedure where diabatic transformation is carried out *only* in the region of a sharp avoided crossing. A similar procedure for making local diabatic transformation has been discussed by Christensen-Dalsgaard (1984). Our procedure differs from hers and we do not need to calculate $P_{\mu\nu}(R)$ over dense mesh points even in the sharp avoided crossing region. This method is described in section 2. In section 3 it is applied to the adiabatic potential curves of He calculated in hyperspherical coordinates. We show that all the off-diagonal coupling terms in the diabatic basis are small and the diabatic wavefunctions evolve smoothly with R . The limitation of this method and alternative approaches are discussed in section 4.

2. Theoretical method

Consider two adiabatic curves which have a sharp avoided crossing between R_1 and R_2 (see figure 1). The goal is to find a procedure such that a pair of diabatic curves can be constructed within this interval. In the present context, we use diabatic to describe states that are not adiabatic and that two diabatic potential curves cross. In contrast to the more strict definition (Smith 1969) the $P_{\mu\nu}(R)$ is not required to vanish within the $[R_1, R_2]$ interval, but it needs to be small. Thus the conditions for the diabatic states are that the diabatic potential curves are smooth functions of R within the $[R_1, R_2]$ interval and that all coupling terms within the interval are small. The

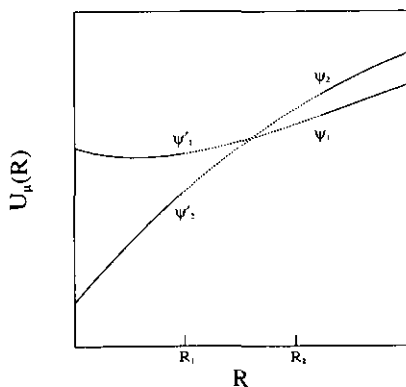


Figure 1. Schematic diagram of an avoided crossing between two adiabatic curves. A local diabatic transformation is to be carried out for the interval $[R_1, R_2]$ shown by broken curves. The adiabatic functions at the two boundary points are defined as indicated.

off-diagonal coupling terms consist of $P_{\mu\nu}$, $Q_{\mu\nu}$ and $U_{\mu\nu}$, where $U_{\mu\nu}$ is the off-diagonal potential matrix $\langle \phi_\mu | H_{01} | \phi_\nu \rangle$.

In figure 1, two adiabatic functions are denoted by ψ_1 and ψ_2 . We also define two functions ψ'_1 and ψ'_2 at $R = R_1$ as shown. When R evolves from R_2 to R_1 , at least one of the adiabatic functions at R_1 has to change its sign since θ becomes $\pi/2$ in crossing the region (see equation (9)). Thus, we have $\psi'_1(R_1; r) = \mp \psi_2(R_1; r)$ and $\psi'_2(R_1; r) = \pm \psi_1(R_1; r)$, where the upper signs are for $P_{12}(R) > 0$ and the lower signs for $P_{12}(R) < 0$. In defining the new diabatic states we require that the diabatic states and the adiabatic states coincide at the boundaries R_1 and R_2 . Define two new functions

$$F_1(r) = \frac{\psi_1(R_2; r) + \psi'_1(R_1; r)}{2N_1} \quad F'_1(r) = \frac{\psi_1(R_2; r) - \psi'_1(R_1; r)}{2N'_1} \quad (11a)$$

and

$$F_2(r) = \frac{\psi_2(R_2; r) + \psi'_2(R_1; r)}{2N_2} \quad F'_2(r) = \frac{\psi_2(R_2; r) - \psi'_2(R_1; r)}{2N'_2}. \quad (11b)$$

From the definition, it is obvious that F_i is the mean of the two diabatic functions at the boundaries and F'_i is the difference. The N in (11a, b) are normalization constants:

$$N_i = \frac{(1 + \langle \psi_i | \psi'_i \rangle)^{1/2}}{\sqrt{2}} \quad N'_i = \frac{(1 - \langle \psi_i | \psi'_i \rangle)^{1/2}}{\sqrt{2}}. \quad (11c)$$

The procedure is to construct diabatic states within the $[R_1, R_2]$ interval from the adiabatic functions defined at R_1 and R_2 :

$$\begin{aligned} \phi_1(R; r) &= [\cos \alpha_1(R)F_1 + \sin \alpha_1(R)F'_1 + C_1(R)\psi_2 + C'_1(R)\psi'_2] / M_1(R) \\ \phi_2(R; r) &= [\cos \alpha_2(R)F_2 + \sin \alpha_2(R)F'_2 + C_2(R)\psi_1 + C'_2(R)\psi'_1] / M_2(R) \end{aligned} \quad (12)$$

where R -dependent functions are explicitly indicated and M_1 and M_2 are normalization constants. The R -dependent functions α and C are arbitrary except that they are to result in smooth potential curves and small coupling terms in the interval $[R_1, R_2]$. They are also chosen such that the wavefunctions and the coupling matrices join smoothly with those calculated from the adiabatic representation at the boundaries R_1 and R_2 .

We illustrate the procedure for the construction of ϕ_2 .

(i) Continuity at $R = R_2$:

$$\phi_2(R_2) = \psi_2(R_2).$$

This condition gives

$$C_2(R_2) = 0 \quad (13a)$$

$$C'_2(R_2) = 0 \quad (13b)$$

$$\alpha_2(R_2) = \tan^{-1}(N'_2/N_2). \quad (13c)$$

(ii) Continuity at $R = R_1$:

$$\phi_2(R_1) = \psi'_2(R_1).$$

This condition gives

$$C_2(R_1) = 0 \quad (14a)$$

$$C'_2(R_1) = 0 \quad (14b)$$

$$\alpha_2(R_1) = -\alpha_2(R_2). \quad (14c)$$

(iii) Continuity of R -dependent derivatives at $R = R_2$,

$$P_{12}^d(R_2) = P_{12}^a(R_2) \quad (15a)$$

$$W_{22}^d(R_2) = W_{22}^a(R_2) \quad (15b)$$

$$\frac{d}{dR} W_{22}^d(R_2) = \frac{d}{dR} W_{22}^a(R_2) \quad (15c)$$

where the superscript d and a refer to matrix elements calculated with diabatic basis functions and adiabatic basis functions, respectively. A similar set of equations can be obtained at $R = R_1$.

We chose to expand $C_2(R)$, $C_2'(R)$ and $\alpha_2(R)$ in polynomials of $(R - R_1)$ in the interval $[R_1, R_2]$. By making the additional auxiliary condition that

$$dC_2(R_1)/dR = 0 \quad (16a)$$

one can express $C_2(R)$ in the form

$$C_2(R) = \frac{(R - R_1)^{2.5}}{(R_2 - R_1)^{2.5}} \left[(R - R_2) \frac{dC_2(R_2)}{dR} + \frac{(R - R_2)^2}{2} \frac{d^2C_2(R_2)}{dR^2} \right] \quad (17a)$$

such that the boundary conditions (13a) and (13b) are satisfied. The derivatives at $R = R_2$ inside the square bracket are obtained from solving (15a-c) and thus can be expressed in terms of non-adiabatic coupling terms calculated at $R = R_2$. In (17a), a power of 2.5 was chosen since it gives the best behaved coupling terms, but its precise value is not important so long that it is greater than 2 such that the boundary conditions for the C and their derivatives are satisfied.

By imposing an auxiliary condition that

$$dC_2'(R_2)/dR = 0 \quad (16b)$$

one can obtain a similar expression for $C_2'(R)$

$$C_2'(R) = \frac{(R_2 - R)^{2.5}}{(R_2 - R_1)^{2.5}} \left[(R - R_1) \frac{dC_2'(R_1)}{dR} + \frac{(R - R_1)^2}{2} \frac{d^2C_2'(R_1)}{dR^2} \right] \quad (17b)$$

where the derivatives inside the square bracket are similarly solved in terms of non-adiabatic coupling terms at $R = R_1$.

Finally the angle $\alpha_2(R)$ can be expanded in the form

$$\alpha_2(R) = d_1 + d_2(R - R_1) + d_3(R - R_1)^2 + d_4(R - R_1)^3 \quad (17c)$$

where the coefficients d_1 and d_2 are solved from the boundary conditions (13c) and (14c) and d_3 and d_4 are solved from (15a-c) in terms of the non-adiabatic coupling terms at $R = R_2$.

We emphasize that this method, as seen from the equations above, does not use any non-adiabatic coupling terms within the interval $[R_1, R_2]$.

3. Applications to the adiabatic hyperspherical potentials of He

3.1. Coupling terms between two diabatic functions

We illustrate the procedure above by performing a diabatic transformation on the hyperspherical potential curves of He. Among the three $1P^o$ curves that converge to

the $\text{He}^+(N=2)$ limit, it is known that the + and - curves (labelled 2 and 3, respectively, in figure 3) have a sharp avoided crossing at $R \approx 7.4$ (Macek 1968, Lin 1986). This avoided crossing results in a sharp $P_{\mu\nu} = \langle \psi_\mu | d/dR | \psi_\nu \rangle$ and large second-order diagonal coupling terms $W_{\mu\mu} = \langle \psi_\mu | d^2/dR^2 | \psi_\mu \rangle$ for each channel. In figure 2(a) and (b) we show these two matrix elements calculated in the adiabatic basis (in full curves) and in the diabatic basis (in broken curves).

The local diabatic transformation is carried out between $R_1 = 6.75$ and $R_2 = 8.10$. The resulting $P_{\mu\nu}$ and $W_{\mu\mu}$ (for $\mu = 2, \nu = 3$ of figure 3) from the diabatic basis functions are shown as broken curves in figure 2(a) and (b). It is clear that the coupling terms in the diabatic representation are reduced significantly.

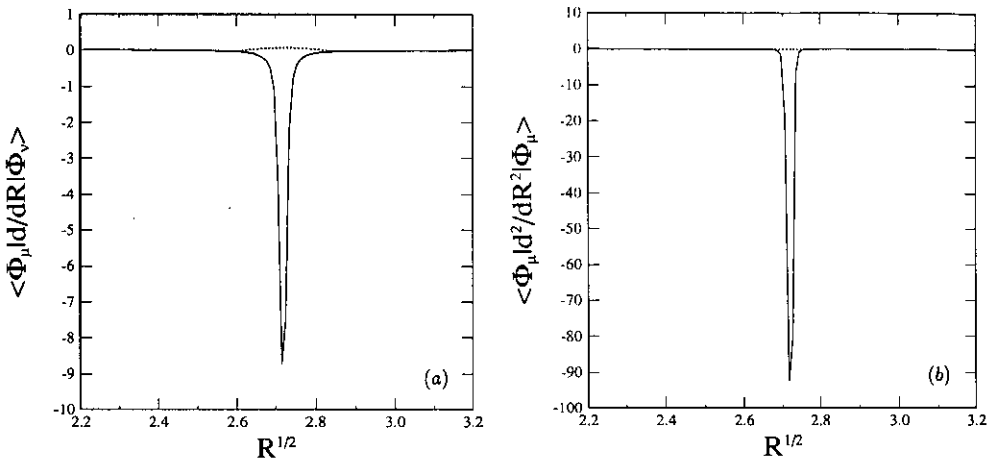


Figure 2. (a) The first-order coupling matrix $P_{\mu\nu}(R)$ between the $(\mu, \nu) = (2, 3)$ channels for the $^1P^o$ states of He (see text). The full curve refers to adiabatic basis states and the broken curve to diabatic basis states. The couplings differ only in the crossing region $[R_1, R_2]$. (b) Same as (a) except for the diagonal $W_{\mu\mu}$ term for $\mu = 3$.

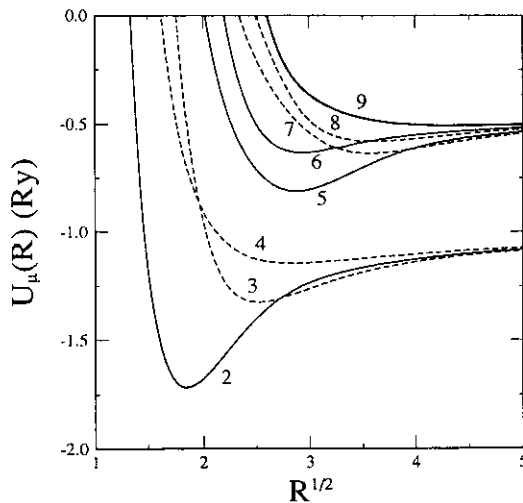


Figure 3. Diabatic potential curves for the $^1P^o$ channels of He that converge to the $N = 2$ and $N = 3$ thresholds of He^+ . The $\mu = 1$ channel is not shown.

The diabatic potential curves for the $1P^\circ$ channels of He below the $N=2$ and $N=3$ thresholds of He^+ constructed using the present procedure are shown in figure 3 where an index ν is used to label each diabatic potential curve, with $\nu=1$ being the lowest channel converging to the $\text{He}^+(N=1)$ threshold (not shown). We mention that each channel can be classified using the K , T and A quantum numbers (Lin 1986), but the precise classification of channels is not important for the present purpose.

The present diabatic transformation procedure gives smooth diabatic potentials. However, in a single channel approximation the hyper-radial wavefunctions are calculated from an effective potential including the contribution from the second-order diagonal term $W_{\mu\mu}$. If such effective potentials are plotted against $R^{1/2}$, as shown in figure 4, the curves still display small kinks in the $[R_1, R_2]$ region. The inset in this figure gives an expanded view of this region. On the other hand, the kinks are quite small and are not 'visible' to the resonance states where the typical wavelength of each resonance is much larger than the range $R_2 - R_1$.

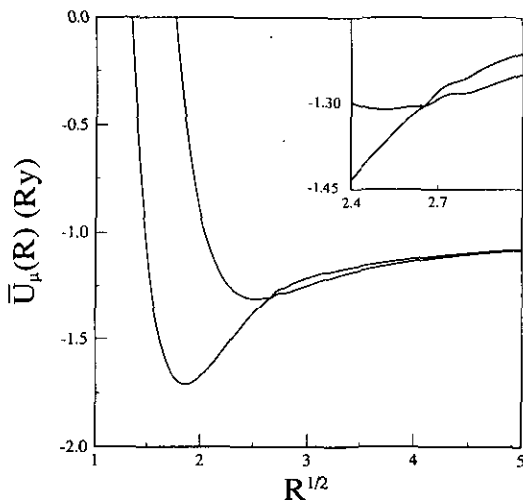


Figure 4. The effective potential, $\bar{U}_\mu(R) = U_\mu(R) + W_{\mu\mu}(R)$, for the $\mu=2$ and $\mu=3$ channels. The small kinks near the crossing region are due to the structure in the $W_{\mu\mu}$ term. The inset displays the crossing region in more details.

We examine further the coupling terms between the $\mu=2$ and $\nu=3$ channels (referring to the label in figure 3). We see from figure 2(a) that P_{23} has a peak value of -9.0 in the adiabatic basis, but only 0.1 in the diabatic basis. A more clear display of the P_{23} in the diabatic basis is shown in figure 5(a) and the second-order diagonal term Q_{23} is given in figure 5(b). The off-diagonal $U_{23}(R)$ is non-zero only in the $[R_1, R_2]$ region and is shown in figure 5(c). These figures show that all the off-diagonal coupling terms are small and can be neglected in a first-order single channel approximation. However, all of them still show non-monotonic variations with R .

3.2. R -dependence of diabatic wavefunctions

Besides the coupling terms, one can also compare the variation of the adiabatic versus the diabatic wavefunctions in the $[R_1, R_2]$ region. For this purpose we calculate the electronic density function on the (α, θ_{12}) plane, where the two angles measure the

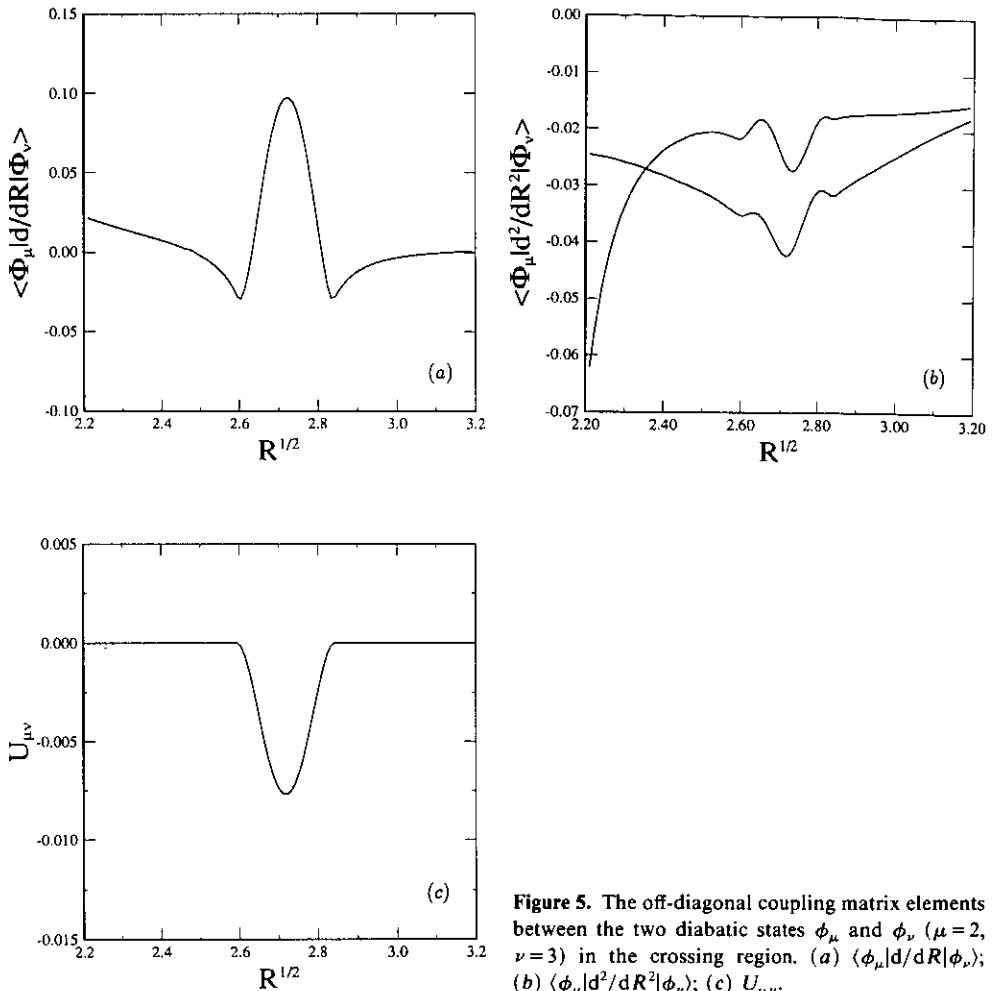


Figure 5. The off-diagonal coupling matrix elements between the two diabatic states ϕ_μ and ϕ_ν ($\mu=2$, $\nu=3$) in the crossing region. (a) $\langle \phi_\mu | d/dR | \phi_\nu \rangle$; (b) $\langle \phi_\mu | d^2/dR^2 | \phi_\nu \rangle$; (c) $U_{\mu\nu}$.

relative radial and angular coordinates of the two electrons (Lin 1984). This is done at each R by averaging over the rotation of the whole atom. In figure 6(a), in the left- and in the right-hand columns, the density functions for the two adiabatic channels ($\nu=2, 3$ of figure 3) are shown for $R=8.10, 7.76, 7.43, 7.10$ and 6.73 (counted from the top), respectively. It is clear that the adiabatic functions do not preserve the density distributions within this interval. In fact, the last frame in the second column is closer to the one on the top in the first column, and the density plots vary rapidly in the interval. In figure 6(b) we show the density distributions of the diabatic states. It is clear that these density distributions evolve smoothly with R .

3.3. Non-adiabatic couplings between pairs of channels belonging to different manifolds

The diabatic transformation discussed above has been used to treat the potential curves of $^1P^o$ doubly excited states of He, as shown in figure 3. In this subsection we discuss the coupling terms of the $\nu=2$ channels with all the five channels of the $N=3$ manifold. According to the $(K, T)_N^A$ classification scheme, (Lin 1984) the $\nu=2$ channel is designated as $(0, 1)_2^+$ and the $\nu=5$ channel as $(1, 1)_3^+$. The wavefunctions of these two

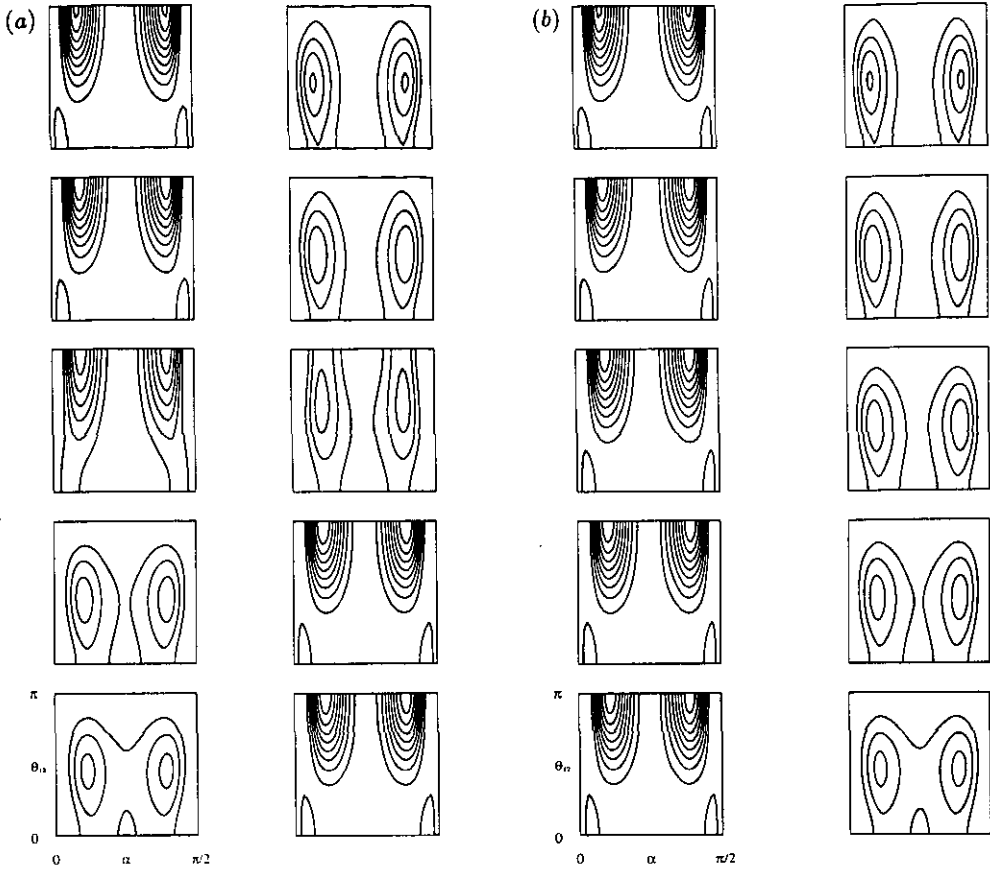


Figure 6. (a) Electron density distributions on the (α, θ_{12}) plane for the two adiabatic channels in the crossing region. The left-hand column is for the $\mu=2$ channel and the right-hand column for the $\mu=3$ channel. The values of R , from the top, are 8.10, 7.76, 7.43, 7.10 and 6.73, respectively. (b) same as (a) but for the diabatic states obtained from the local transformation procedure.

channels are similar and one expects that the coupling terms between them be larger than the couplings of the $\nu=2$ channel with other channels in the $N=3$ manifold.

In figure 7(a) the $P_{2\mu}$ for $\mu=5-9$ are shown. The full curve is for P_{25} which is much larger than other couplings. However, the coupling between the $\mu=2$ and 6 channels (chain curves) is not very weak. The $\nu=6$ channel is classified as $(-1, 1)_3^+$. It is clear that only channels with the same A quantum number have larger coupling terms. The other three channels are labelled as $(2, 0)_3^-$, $(0, 0)_3^-$ and $(-2, 0)_3^0$ for $\nu=7, 8$ and 9 respectively. These channel functions have rather different nodal structure from the $\nu=2$ channel and thus the coupling terms are small.

In the diabatic basis set, the off-diagonal potential matrix elements are non-zero. In figure 7(b) we show the ratio of the off-diagonal matrix element $U_{\mu\nu}$ with respect to the difference of $U_\mu - U_\nu$. Again the ratio is largest for $(\mu, \nu) = (2, 5)$ and the rest are much weaker. This result, together with those shown in figure 7(a), indicate that in a coupled-channel calculation the coupling between the $\nu=2$ and $\nu=5$ channel is the most important one and coupling of the $\nu=2$ channel with other channels may

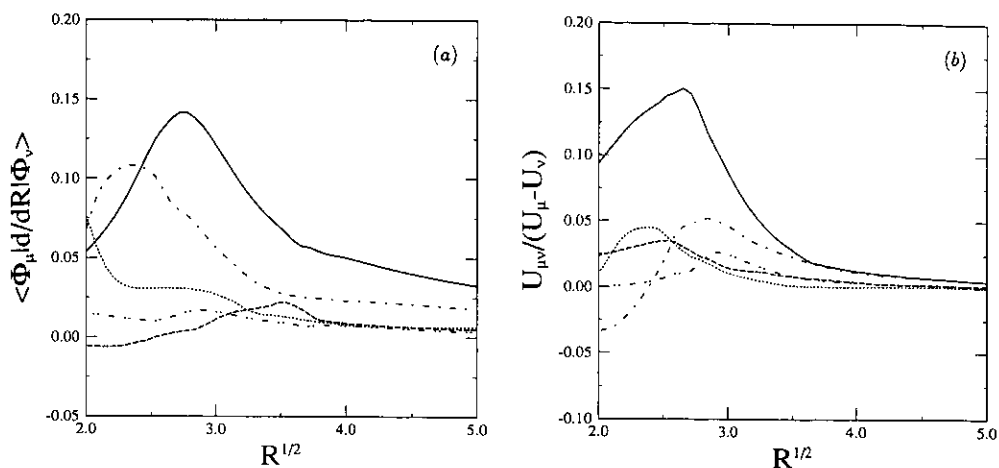


Figure 7. First-order coupling terms $P_{\mu\nu}(R)$ for $\mu=2$ and the five channels belonging to the $N=3$ manifold. The dominant coupling is with the $\nu=5$ channel, and is given by a full curve. The other channels are with the $\nu=6$ (chain curves), $\nu=7$ (dotted curves), $\nu=9$ (double chain curves) and $\nu=8$ (broken curves). (b) Ratios of $U_{\mu\nu}/(U_{\mu} - U_{\nu})$ for $\mu=2$ and $\nu=5-9$. The notations for different ν are identical to those given in (a).

be neglected in the first-order calculation. Such coupled-channel calculations are currently underway.

4. Summary and discussion

In this article we illustrate a local diabatic transformation procedure to a pair of adiabatic states. Unlike the previous methods where diabatic transformation was carried out over the whole range of R , this method performs diabatic transformation only in the region of sharp avoided crossing, thus preserving the global character of the adiabatic approach. After this diabatic transformation is carried out, it is shown that all of the remaining off-diagonal coupling terms are small, and the wavefunction of each diabatic channel does evolve 'adiabatically' with R and that diabatic functions preserve the nodal structures.

The present local diabatic transformation has one important advantage over other approaches. Since the precise values of $P_{\mu\nu}$ between the two adiabatic states are not used in the transformation, there is no need to calculate $P_{\mu\nu}$ over dense mesh points in the avoided crossing region. However, the present approach still has a number of shortcomings. First, the residual coupling terms, while are small in the crossing region, exhibit relatively non-monotonic behaviour. It is not clear whether different choices of the fitting functions (see (17)) can remove such structures. Second, the present procedure only applies to avoided crossings between two channels. If three or more channels have to be treated together in a local region, the present method can be generalized but it would be more tedious to do. For many-channel problems, the diabatic-by-sector method (Pack and Parker 1987, Launay and Le Dourneuf 1989, 1990, Light and Walker 1976) employed by practitioners in atom-molecule reactive scattering may be preferable.

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References

- Christensen-Dalsgaard B L 1984 *Phys. Rev. A* **29** 470
Delos J B and Thorson W R 1978 *Phys. Rev. A* **18** 117
Gabriel H and Taulbjerg K 1974 *Phys. Rev. A* **10** 741
Garrett B C and Truhlar D G 1981 *Theoretical Chemistry: Advances and Perspectives* vol 6A ed D Hendersen (New York: Academic) p 215
Heil T G, Butler S E and Dalgarno A 1981 *Phys. Rev. A* **23** 1100
Kimura M and Lane N F 1990 *Adv. At. Mol. Phys.* **26** 79
Launay J M and Le Dourneuf M 1989 *Chem. Phys. Lett.* **163** 178
— 1990 *Chem. Phys. Lett.* **169** 473
Light J C and Walker R B 1976 *J. Chem. Phys.* **65** 4272
Lin C D 1984 *Phys. Rev. A* **29** 1019
— 1986 *Adv. At. Mol. Phys.* **22** 77
Macek J H 1968 *J. Phys. B: At. Mol. Phys.* **1** 831
Pack R T and Parker G A 1987 *J. Chem. Phys.* **87** 3888
Smith F T 1969 *Phys. Rev.* **179** 111
Tan J and Lin C D 1988 *Phys. Rev. A* **37** 1152