Theor Chim Acta (1990) 77: 333–341

Theoretica Chimica Acta

Predissociation lifetime of the $1\sigma_g^2 2\sigma_g$ diabatic state of He_2^+: a one-channel approach

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Received August 10, 1989; received in revised form December 4, 1989/Accepted February 23, 1990

Summary. This work is concerned with the application of a one-channel model to obtaining predissociation lifetimes and transition rates in a system of crossing diabatic states. The calculation focuses on the first shape resonance of the $1\sigma_g^2 2\sigma_g$ diabatic state of He_2^+, which is relatively stable with respect to tunneling. This resonance predissociates as a result of the $1\sigma_g^2 2\sigma_g$ state being crossed by the $1\sigma_g 1\sigma_u^2$ dissociative diabatic state near the resonance level. We have estimated its predissociation lifetime to be of the order of 10^{-11} s.

Key words: Diabaticity – Predissociation – Lifetime – He_2^+

Introduction

The importance of the series of avoided crossings among the potential curves of the ${}^2\Sigma_g^+$ system of He_2^+ has been known for many years. They are intimately involved in the interpretation of various features of the elastic, inelastic and charge transfer collision cross sections of $He(1s^2)$ with $He^+(1s)$ [1].

As the internuclear distance (R) of the above system decreases, the initially degenerate ground state separates into two diabatic states. The lower of the two is the $1\sigma_g^2 1\sigma_u$ and the higher is the $1\sigma_g 1\sigma_u^2$ state. The lower state goes on to become the ${}^2\Sigma_u^+$ ground adiabatic state of the ion. The higher state is crossed at $R_x \approx 1.45\, a_0$ by the $1\sigma_g^2 2\sigma_g$ diabatic state, which dissociates into $He^+(1s) + He(1s2s)$ [2, 3]. Because of the non-crossing rule, in an actual adiabatic calculation of their potential energy curves the crossing of these two g states becomes an avoided crossing of the corresponding $1\,{}^2\Sigma_g^+$ and $2\,{}^2\Sigma_g^+$ adiabatic states, the character of which interchanges around this point [2]. Similar avoided crossings are generated in the adiabatic calculation of higher ${}^2\Sigma_g^+$ states because the $1\sigma_g 1\sigma_u^2$ state crosses higher $1\sigma_g^2 n\sigma_g$ ($n = 2, 3, \ldots$) diabatic states [1, 2].

The interpretation of the above mentioned experimental data requires that the system has a small transition probability out of the $1\sigma_g 1\sigma_u^2$ state as R decreases [3]. It is therefore of interest to calculate such a probability. To do this, one must at least construct all the diabatic potentials that constitute open channels for a given collision energy from an equal number of computed adiabatic potentials [4]. Then, using the diabatic potential matrix so constructed, one can integrate the Schrödinger equation and obtain the S matrix from which the transition probabilities may be obtained.

However, if one is interested only in an order of magnitude estimate of the above probability, a simpler approach may be applicable. It has been shown [5] that under certain conditions it is possible to ignore the quantum interference effects and treat the problem by a one-channel model. Within this approximation, one constructs only those pairs of diabatic states which cross in the vicinity of the collision energy, and computes the predissociation widths at each crossing either by a Landau–Zener type formula or by a golden rule expression as suggested by van Dischoek et al. [6]. This procedure stops when a width below or near an acceptable tolerance is reached. A total width is obtained by adding the computed partial widths; the total lifetime and transition rate are then computed from the total width.

As a first step towards applying these methods in exploring the details of this system of crossing diabatic states, we perform here a restricted one-channel calculation at the energy of the first shape resonance of the $1\sigma_g^2 2\sigma_g$ diabatic state of He_2^+. We aim to obtain an order of magnitude estimate of the predissociation lifetime of this resonance as well as an order of magnitude estimate of the transition rate out of the $1\sigma_g 1\sigma_u^2$ state, at a collision energy in the neighborhood of the resonance energy. These two crossing diabatic states are constructed by an orthogonal transformation of the $1\,{}^2\Sigma_g^+$ and $2\,{}^2\Sigma_g^+$ adiabatic states [7]. Their crossing is the first of an infinite number of such crossings, but it is separated by about 6.75 eV from the rest of them. Because of this separation, the partial widths from the higher crossings are expected to be very small, and they are ignored in this work.

Theoretical framework

The adiabatic to diabatic transformation we employ here [7] is well known. It has been applied even in the absence of accurate coupling strengths [8], as well as in vibrational energy transfer under a model analogous to the Born–Oppenheimer approximation [9]. Thus, we only sketch the main points of the theory as it applies to a diatomic molecule.

Let $\boldsymbol{\phi}(\boldsymbol{r}; R)$ be the column vector of the adiabatic electronic eigenfunctions of the diatom, and let $\boldsymbol{\chi}(R)$ be the column vector of the corresponding radial eigenfunctions. $\boldsymbol{r}$ is the vector of the electronic coordinates. For simplicity, we have neglected the angular motion since we are concerned only with radial couplings. Then, the total wavefunction is

$$\Psi(\boldsymbol{r}, R) = \boldsymbol{\phi}^+(\boldsymbol{r}, R) \cdot \boldsymbol{\chi}(R). \tag{1}$$

The Schrödinger equation for the radial wavefunctions of the diatom in the adiabatic representation is given by the following well-known relation:

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}\mathbb{I} - \mathbb{V}(R) + E\,\mathbb{I} + \frac{\hbar^2}{2\mu}\left[2\mathbb{A}(R)\frac{d}{dR} + \mathbb{B}(R) \right] \right) \boldsymbol{\chi}(R) = 0, \tag{2}$$

where $\mathbb{I}$ is the unit matrix, $\mathbb{V}$ is the diagonal potential matrix corresponding to $\boldsymbol{\phi}$, E is the total energy and $\mathbb{A}$ and $\mathbb{B}$ are the matrices of the vibronic (radial) coupling strengths. That is,

$$A(R)_{ij} = \langle \phi_i | d/dR | \phi_j \rangle \quad \text{and} \quad B(R)_{ij} = \langle \phi_i | d^2/dR^2 | \phi_j \rangle.$$

If Eq. (2) is to be solved by the usual methods—which assume the absence of the first derivative term—a transformation to a diabatic representation must be done. Let $\mathbb{C}(R)$ be such a transformation matrix. One needs as complete a separation between the electronic and nuclear functions as possible. Thus, one may write

$$\boldsymbol{\phi}(\boldsymbol{r}; R) = \mathbb{C}(R)\boldsymbol{\eta}(\boldsymbol{r}; R_0), \tag{3a}$$

$$\boldsymbol{\chi}(R) = \mathbb{C}(R)\boldsymbol{\zeta}(R), \tag{3b}$$

where $\boldsymbol{\eta}(\boldsymbol{r}; R_0)$ is a new diabatic basis evaluated at a given internuclear distance R_0, and $\boldsymbol{\zeta}(R)$ is the new nuclear function containing all the R dependence of $\Psi(\boldsymbol{r}; R)$. The total wavefunction must be the same in either representation. That is, one must have

$$\Psi(\boldsymbol{r}; R) = \boldsymbol{\eta}^+(\boldsymbol{r}; R_0) \cdot \boldsymbol{\zeta}(R).$$

This means that one should expect that $\mathbb{C}^+ \cdot \mathbb{C} = \mathbb{I}$ (see below). Substituting Eq. (3) into Eq. (2) gives

$$\mathbb{C}\frac{d^2}{dR^2}\boldsymbol{\zeta} + 2\left(\frac{d}{dR}\mathbb{C} + \mathbb{A}\cdot\mathbb{C}\right)\frac{d}{dR}\boldsymbol{\zeta} + \mathbb{U}\cdot\mathbb{C}\boldsymbol{\zeta} + \left(\mathbb{B} + \frac{d^2}{dR^2} + \mathbb{A}\frac{d}{dR}\right)\mathbb{C}\boldsymbol{\zeta} = 0,$$

where $\mathbb{U}(R) = -(2\mu/\hbar^2)(\mathbb{V}(R) - E\,\mathbb{I})$. The matrix $\mathbb{C}$ is now determined by the requirement that the first derivative term be identically zero. Thus, one must solve the following equation:

$$\frac{d}{dR}\mathbb{C}(R) + \mathbb{A}(R)\cdot\mathbb{C}(R) = 0. \tag{4}$$

The requirement represented by Eq. (4) has two consequences: (i) the solution matrix $\mathbb{C}(R)$ is indeed orthogonal (see appendix 2 of [7]), and (ii) for a *complete* adiabatic basis $\boldsymbol{\phi}(\boldsymbol{r}; R)$, it follows that

$$\left(\mathbb{B} + \frac{d^2}{dR^2} + 2\mathbb{A}\frac{d}{dR}\right)\cdot\mathbb{C}$$

vanishes identically (see appendix B of [9]). Then, neglecting the above term (even though the basis is not complete) Eq. (2) finally becomes

$$\mathbb{I}\frac{d^2}{dR^2}\boldsymbol{\zeta}(R) + \mathbb{W}(R)\boldsymbol{\zeta}(R) = 0, \tag{5}$$

where

$$\mathbb{W}(R) = \mathbb{C}^+(R)\cdot\mathbb{U}(R)\cdot\mathbb{C}(R). \tag{6}$$

For a two state model one may parameterize the orthogonal matrix $\mathbb{C}$ with a sin/cos pair [7]:

$$\mathbb{C}(R) = \begin{bmatrix} \cos\theta(R) & \sin\theta(R) \\ -\sin\theta(R) & \cos\theta(R) \end{bmatrix}. \tag{7}$$

Substituting Eq. (7) into Eq. (4), $\theta(R)$ may be determined in terms of the $A_{12}(R)$

matrix elements:

$$\begin{bmatrix} -\sin\theta & \cos\theta \\ -\cos\theta & -\sin\theta \end{bmatrix} \frac{d\theta}{dR} = \begin{bmatrix} 0 & A_{12} \\ -A_{12} & 0 \end{bmatrix} \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}.$$

This leads to

$$\theta(R) = \int_{R_0}^{R} A_{12}(R')\,dR', \tag{8}$$

where R_0 is the beginning of the A_{12} curve. Once θ is determined, $\mathbb{W}(R)$ is given by Eq. (6), and it is no longer a diagonal matrix:

$$\begin{aligned} W_{11}(R) &= V_{11}(R)\cos^2\theta(R) + V_{22}(R)\sin^2\theta(R), \\ W_{22}(R) &= V_{11}(R)\sin^2\theta(R) + V_{22}(R)\cos^2\theta(R), \\ W_{12}(R) &= (V_{11}(R) - V_{22}(R))\sin\theta(R)\cos\theta(R). \end{aligned} \tag{9}$$

Since $\boldsymbol{\eta}(\mathbf{r}, R_0)$ are not eigenfunctions of the electronic hamiltonian, the diagonal terms of $\mathbb{W}$ cross at some point R_x having energy E_x; the off diagonal terms represent the interaction among the diagonal terms around this point.

Methodology and results

As mentioned earlier, the vibronic coupling strengths, $A_{12}(R)$ between the two lowest ${}^2\Sigma_g^+$ adiabatic states of He_2^+ have been computed previously by a finite differences method [2]. Of necessity, only a small number of points near the avoided crossing have been computed. Let us denote by R_i and R_f the first and last of these points respectively. A_{12} is very close to zero at these points, and it has been assumed that $A_{12} = 0$ for $R > R_f$ and $R < R_i$. This assumption is justified because sample calculations in this region have given nearly zero coupling strengths. Although A_{12} has a Lorenzian shape, it has been fitted by a segmented quadratic spline method, and 6000 points have been generated between the end points R_i and R_f from the coefficients of the fit. Using $R_0 = R_i$, the integration in Eq. (8) has been carried out in steps of six points by the trapezoid rule, giving a numerical representation of 1000 points for $\theta(R)$. The $2\,{}^2\Sigma_g^+$ state has been fitted by a segmented quadratic spline, while for the $1\,{}^2\Sigma_g^+$ state a segmented cubic spline fit has been used. In all the above fits, only the constraint of function equality at the segment joints has been enforced, and not equality of first or second derivatives.

Now, it is well known that the area under the $A_{12}(R)$ curve must be equal to $\pi/2$ for couplings due to variations of the CI coefficients, which is the case here. However, due to the limited number of calculated coupling strengths, and due to inaccuracies in their calculation as well as the fact that the integration can be carried out only between R_i and R_f, the area under this curve is not $\pi/2$ in practice. This generates difficulties in the calculation of the diabatic potential curves since at the end of the integration $\sin\theta \neq 1$ and $\cos\theta \neq 0$. To counterbalance this, a correction has been made at each of the 1000 points of $\theta(R)$. First, the total area, θ_t, under the A_{12} curve has been obtained by an initial integration of A_{12} between its end points. Then, the nth point obtained from the integration in Eq. (8), as described above, has been corrected by adding $n(\pi/2 - \theta_t)/1000$ to it. For the fit used for A_{12}, the correction $\pi/2 - \theta_t$ is quite small, and it causes the diabatic curves to behave correctly; its effect on the transition rate is expected to be minimal.

The potential curve of the $1\sigma_g 1\sigma_u^2$ diabatic state generated as above is repulsive. On the other hand, the $1\sigma_g^2 2\sigma_g$ curve has a barrier and it can support a few shape resonances. The descent of the potential from the top of the barrier is very slow, making the barrier quite broad. Consequently, the first of these resonances is expected to be relatively stable as far as barrier penetration is concerned. Its width, Γ_S, is expected to be very small compared to the width of the Feshbach resonance, Γ_F, generated by the crossing of these two diabatic states. To calculate the radial wavefunctions we employ the Numerov integration method [10, 11]. Strictly speaking, since the Numerov method cannot be applied to resonances, a complex rotation method should have been used [12]; however, since we are interested only in an order of magnitude estimate, and assuming $\Gamma_S \ll \Gamma_F$, we have approximated the potential beyond the top of the barrier by a straight line parallel to the R axis. This slight modification of the potential has converted it into a bound one, and has enabled us to calculate approximate energies by a variation of the Numerov method due to Hajj [10]. The position of the first shape resonance along with the corresponding radial wavefunction are not expected to change much because of this approximation.

As shown below, both the "bound" and the continuous wavefunction as well as W_{12} are used in a golden rule expression. Therefore, the Numerov integration must be done with the same mesh of points for both states. A uniform mesh with a step size $\Delta R = 4 \times 10^{-4}\, a_0$ has been established in the integration of Eq. (8), and the actual computation of W_{11}, W_{22} and W_{12} has been done only between the end points of A_{12} on this mesh. Outside this region, on a mesh generated with the same step size, we have set $W_{12} = 0$. For $R < R_i$ we have set $W_{11} = V_{11}$ and $W_{22} = V_{22}$ while for $R > R_f$ we have set $W_{11} = V_{22}$ and $W_{22} = V_{11}$. Figure 1 shows the resulting diabatic potentials, including the approximated tail end of the quasibound one, the approximate position of the first resonance, and the *ab initio* points of the adiabatic potentials [2]. Table 1 shows a few selected values of the interaction W_{12}.

Table 1. Representative values of the interaction W_{12} between R_i and R_f

R (a_0)	W_{12} (a.u.)
1.25033	0.00007
1.29033	0.00814
1.33033	0.01577
1.37033	0.02063
1.41033	0.02615
1.44993	0.03415
1.49033	0.02595
1.53033	0.02112
1.57033	0.01633
1.61033	0.00837
1.64953	0.00008

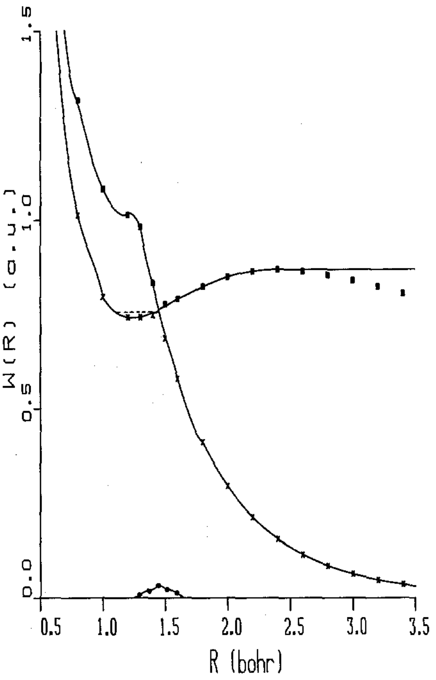

Fig. 1. The potentials involved in the calculation: ——, the $1\sigma_g 1\sigma_u^2$ repulsive diabatic potential W_{11}, and the modified $1\sigma_g^2 2\sigma_g$ quasibound diabatic potential W_{22}; —●—, the interaction potential W_{12}; —■— *ab initio* points for the $2\,^2\Sigma_g^+$ adiabatic potential; —×— *ab initio* points for the $1\,^2\Sigma_g^+$ adiabatic potential; ----- the approximate energy level of the first resonance

Once the diabatic potentials are computed, the Numerov integration over the "bound" state gives the approximate position of the first shape resonance, E_0, and the approximate bound vibrational wavefunction, $\zeta_0(R)$, which is unit normalized. The integration over the repulsive potential at E_0 gives the continuous wavefunction, $\zeta_E(R)$, which is energy normalized by fitting it to the following asymptotic form:

$$\zeta_E(R > R_f) = \left(\frac{2\mu}{\pi k}\right)^{1/2} kR[j_l(kR)\cos\delta_l - \eta_l(kR)\sin\delta_l].$$

where δ_l is the phase shift for orbital angular momentum l (here $l = 0$), $k = (2\mu E_0)^{1/2}$ (in a.u.), j_l and η_l are the spherical Bessel and Hankel functions respectively, and μ is the reduced mass (2.001164×1822.85 a.u.). Figure 2 shows these two normalized wavefunctions.

Now, it is well known that for small perturbations such as W_{12}, the golden rule gives an accurate estimate of the lifetime of a discrete vibrational state of energy E coupled to a bath of continuous states in the vicinity of E. This is also applicable if the initial state is a narrow shape resonance, as is the case here due to the presence of a broad barrier. In the present case, the Fermi Golden Rule expression may be written as follows [6]:

$$k_{12} = \frac{2\pi}{\hbar} |\langle\zeta_E(R)|W_{12}(R)|\zeta_0(R)\rangle|^2.$$

The density of states normally present in the above relation has been absorbed in the energy normalized $\zeta_E(R)$. Converting to atomic units results in

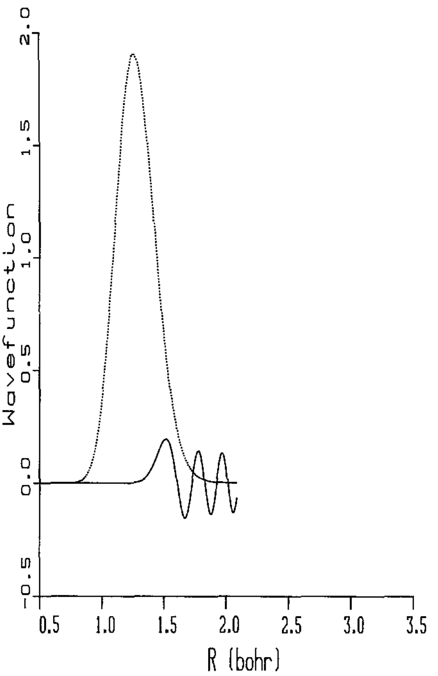

Fig. 2. The normalized wavefunctions used in Eq. (10). They correspond to the diabatic potentials in Fig. 1: . . . . . , the approximate wavefunction of the first resonance; ——, the continuous wavefunction at the energy of the first resonance. These functions extend only to the point where the wavefunction of the first resonance is reliable (see [10])

the expression

$$k_{12} = C_t 2\pi |\langle \zeta_E(R)|W_{12}(R)|\zeta_0(R)\rangle|^2, \tag{10}$$

where $C_t = 1$ and k_{12} is in inverse atomic units of time; for k_{12} in s^{-1} use $C_t = 4.1341 \times 10^{16}$.

The relation (10) is symmetric with regard to the position of the wavefunctions (no derivative is involved as is the case with adiabatic states), and therefore it also gives the transition rate out of the continuous bath of diabatic states around E_0 into the discrete state ζ_0.

Integration of Eq. (10) has been carried out using the trapezoid rule. Of course, because of the way W_{12} has been computed, it is only in the region $R_i < R < R_f$ that the integrand is not zero. The predissociation lifetime and width of the first resonance are given by the usual relations: $\tau_{12} = 1/k_{12}$ and $\Gamma_{12} = \hbar k_{12}$ respectively, where $\hbar = 5.309 \times 10^{-12}\,\mathrm{cm}^{-1}\,\mathrm{s}$ is Planck's constant in the indicated units, so that Γ_{12} is in cm^{-1} if k_{12} is in s^{-1}. A transition rate of the order of $10^{11}\,\mathrm{s}^{-1}$ has been found, which gives a predissociation lifetime of the order of 10^{-11} s. The results are summarized in Table 2.

The transition rate computed here is 10^4 times slower than a similar transition rate between the $2\,^2\Sigma_g^+$ and the $1\,^2\Sigma_g^+$ adiabatic states [13]. This is a result of the strong diabaticity of the system, which can also be seen by a rough Landau–Zener estimate. Such an estimate gives a single pass transition probability between the two diabatic curves of the order of 0.001 to 0.1 for energies in the range of 10^{-5}–10^{-8} a.u. above the crossing point respectively. It is this strong diabaticity that allows one to apply the golden rule as it has been

Table 2. Approximate results of the one-channel calculation. E_m and E_b refer to the energies at the minimum and at the top of the barrier of the $1\sigma_g^2 2\sigma_g$ state (see text for definitions of the other variables). The energies are relative to the ground state asymptote of −4.8983 a.u.

Quantity	Computed result	Units
R_x	1.448	a_0
E_x	0.7604	a.u.
E_0	0.7558	a.u.
E_m	0.7407	a.u.
E_b	0.8680	a.u.
k_{12}	0.84×10^{11}	s^{-1}
τ_{12}	1.2×10^{-11}	s
Γ_{12}	0.445	cm^{-1}

applied here, even though the first shape resonance lies within $2W_{12}$, which is the approximate gap around the avoided crossing of the two adiabatic states. Therefore, working within the *diabatic* approximation, one may take the first shape resonance to be a relatively stable discrete state of the *diabatic* potential. Only a high resolution experiment could reveal the adiabaticity of the system. It is in this sense that the golden rule has been applied here. Notice that similar calculations give predissociation lifetimes of the third, fourth and fifth shape resonances that are within an order of magnitude of the lifetime of the first shape resonance (10^{-10}–10^{-12} s). These resonances lie outside the aforementioned gap.

Conclusion

We have employed an orthogonal transformation to construct the $1\sigma_g 1\sigma_u^2$ and $1\sigma_g^2 2\sigma_g$ diabatic potential curves of He_2^+ and their mutual interaction, starting from the $1\,^2\Sigma_g^+$ and $2\,^2\Sigma_g^+$ adiabatic potential curves and their radial coupling strengths. The crossing of the above two diabatic states gives rise to a Feshbach resonance while the barrier of the $1\sigma_g^2 2\sigma_g$ state gives rise to a shape resonance. Assuming $\Gamma_S \ll \Gamma_F$, we have approximated the shape resonance by a bound vibrational state. Then, via the Numerov algorithm, we have obtained the radial wavefunction and the approximate position of the first "bound" vibrational level of the $1\sigma_g^2 2\sigma_g$ state, as well as the radial wavefunction of the $1\sigma_g 1\sigma_u^2$ state at the same energy level. These functions, along with the diabatic interaction between the two states, have been used in a golden rule expression which has given a predissociation lifetime of the order of 10^{-11} s for the $1\sigma_g^2 2\sigma_g$ state.

Acknowledgements. We thank Prof. C. A. Nicolaides for suggesting the study of the He_2^+ molecular ion. Aspects of this work have been discussed with Prof. R. Lefebvre and Prof. O. Atabek during their visit here, as well as with Dr. N. C. Bacalis.

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