

On the Diabaticity of He_2^+

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The strong diabaticity of the $2\Sigma_g^+$ excited states of He_2^+ has been computationally verified in the region of the well known avoided crossing between the $1^2\Sigma_g^+$ and the $2^2\Sigma_g^+$ adiabatic states. A large transition rate between these two states has been found, which is of the order of 10^{15} sec^{-1} .

Introduction

The system of $2\Sigma_g^+$ excited states of He_2^+ has drawn attention in the past because of its diabaticity, which plays an important role in the interpretation of excitation and electron transfer cross sections in $\text{He}^+ - \text{He}$ collisions [1]. This system is expected to remain in a diabatic state even at relatively low internuclear velocities.

Recently, the six lowest $2\Sigma_g^+$ adiabatic states of He_2^+ as well as the coupling strengths around their numerous avoided crossings have been calculated at the CI level [2]. By following the changes of the coefficients of the CI expansion as well as by inspection of the adiabatic potential curves, a graphical representation of the corresponding diabatic curves has been generated. These curves represent a series of diabatic states $1\sigma_g^2 n\sigma_g$ ($n=2, 3, 4, \dots$) intersected by another series of diabatic states $1\sigma_g 1\sigma_u n\sigma_u$ ($n=1, 2, \dots$), as expected from symmetry considerations [1]. The $1\sigma_g 1\sigma_u^2$ diabatic state is important because it is also the main configuration of the lowest $1^2\Sigma_g^+$ dissociative adiabatic state for internuclear distances (R) larger than about 1.5 Bohr. For R less than about 1.4 Bohr, it becomes the main configuration of the $2^2\Sigma_g^+$ adiabatic state.

It would be of interest to compute the probability of the system remaining in the $1\sigma_g 1\sigma_u^2$ configuration for all R during a $\text{He}^+ - \text{He}$ collision. However, this is a difficult multistate problem because most of these crossings are clustered together. Nonetheless, one may calculate the probability of the system remaining in the said configuration as it moves in the vicinity of the first of these crossings ($R \approx 1.45$ Bohr), which is also

the region of the corresponding avoided crossing between the $1^2\Sigma_g^+$ and the $2^2\Sigma_g^+$ adiabatic states. These states are shown in Figure 1. The above crossing is well separated from the others by a gap of about 6.75 eV, and it may be treated by a two state model. This problem is equivalent to computing the transition rate between the above two adiabatic states in the region of their avoided crossing. The purpose of this paper is to present such a restricted calculation.

Methodology and Results

It is well known that for small perturbations, the probability of a non-adiabatic transition out of a discrete state of energy E , and into a bath of continuum states in the neighborhood of E may be given by the Fermi Golden rule:

$$W = (2\pi/\hbar) |\langle \chi_f | (-\hbar^2/2\mu)(B(R) + 2A(R)\partial/\partial R) | \chi_i \rangle|^2 \varrho(E), \quad (1)$$

where χ_i and χ_f are the initial and final nuclear wavefunctions, respectively, $\varrho(E)$ is the density of states at E and

$$B(R) = \langle \Psi_f | \partial^2/\partial R^2 | \Psi_i \rangle, \quad A(R) = \langle \Psi_f | \partial/\partial R | \Psi_i \rangle. \quad (2)$$

Ψ_i and Ψ_f are the electronic initial and final wavefunctions, respectively, and R is the internuclear distance. The $B(R)$ term usually gives a much smaller matrix element than the $A(R)$ term, and it has been ignored in the following calculations. The computed values of $A(R)$ are shown in Figure 2. They must be fitted to an appropriate function before (3) below can be evaluated.

As it can be seen from Fig. 1, the $2^2\Sigma_g^+$ state has a barrier, and it can support a few quasibound vibrational levels. χ_i may be considered as belonging to the

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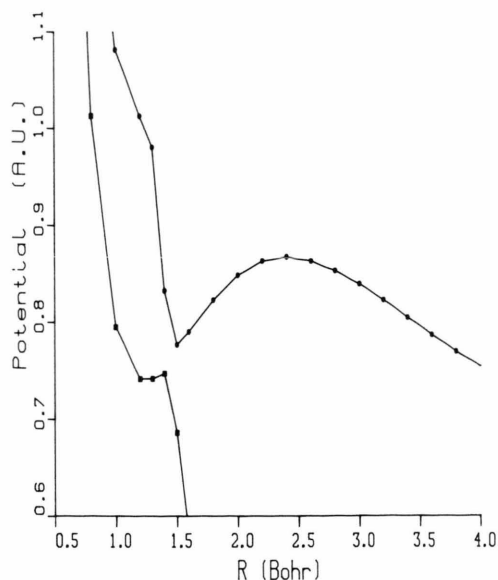


Fig. 1. The two lowest $2\Sigma_g^+$ adiabatic states of He_2^+ around the region of their avoided crossing. The energies are relative to the ground state asymptote (-4.8983 a.u.): —■— $1\ 2\Sigma_g^+$, —●— $2\ 2\Sigma_g^+$. A selected set of their computed values is shown in Table 2 of ref. [2].

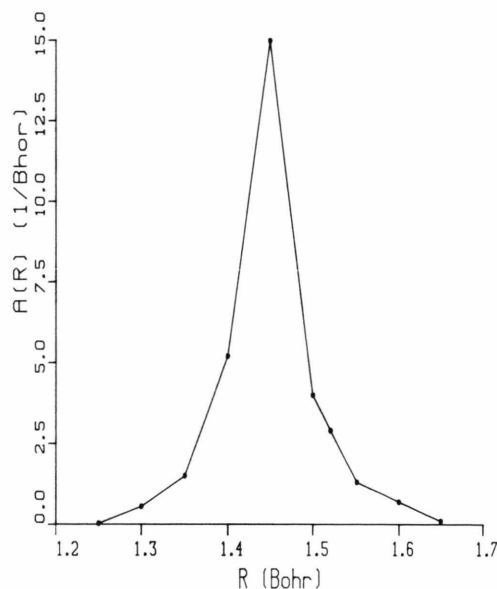


Fig. 2. The vibronic coupling strength ($A(R)$) between the states shown in Fig. 1, as a function of internuclear distance. The computed values are shown in Table 4 of ref. [2].

discrete spectrum of this state for a level near the region where the barrier is relatively wide. Thus, χ_i may be identified with the zeroth vibrational level; henceforth it will be denoted by χ_0 . χ_f belongs to the continuum of the $1\ 2\Sigma_g^+$ state, and it corresponds to a level isoenergetic to that of χ_0 ; henceforth it will be denoted by χ_E . Ignoring $B(R)$ and converting to atomic units, (1) may be written as

$$W = C_1(2\pi/\mu^2) |\langle \chi_E | A(R) \partial/\partial R | \chi_0 \rangle|^2, \quad (3)$$

where for $C_1=1$, W is in inverse atomic units of time while for $C_1=4.1341 \times 10^{16}$, W is given in sec^{-1} . $\varrho(E)$ has been absorbed in χ_E , which is now energy normalized as in (7) below. The reduced mass of the system, μ , is 2.001164×1822.85 a.u. Both functions χ_E and χ_0 are eigenfunctions of the nuclear motion hamiltonians (in a.u.)

$$H = -(1/2\mu) \nabla_R^2 + V_m(R), \quad m=1 \text{ or } 2. \quad (4)$$

$V_1(R)$ and $V_2(R)$ are the potential curves for the two Σ states.

A numerical method, based on the Numerov technique, has been used to compute the transition rate, $K_p(E)$. If one needs to know the lifetimes, $\tau_p(E)$, and width, $\Gamma_p(E)$, of the quasibound state due to the vibronic interaction only, that is excluding barrier

penetration, one can use the well known relations

$$\tau_p(E) = 1/K_p(E), \quad \Gamma_p(E) = \hbar K_p(E), \quad (5)$$

where E refers to the zeroth level energy of χ_0 and p refers to the transition mechanism (predissociation). $\hbar = 5.309 \times 10^{-12} \text{ cm}^{-1} \text{ sec}$ is Planck's constant in the indicated units, so that $\Gamma_p(E)$ is in cm^{-1} if $K_p(E)$ is in sec^{-1} .

χ_0 and χ_E are computed numerically using the well known Numerov integration method [3], which is applicable to all differential equations of the form

$$y''(R) = F(R) y(R). \quad (6)$$

The data points for $A(R)$ and $V_m(R)$ are fitted to cubic polynomials employing a segmented least squares fit procedure under the constraint of equality among the segment functions as well as among their first and possibly second derivatives at each segment joint. However, for $A(R)$ neither the first nor the second derivatives have been matched because its shape does not allow for such a fit.

Following the spline fits of $V_m(R)$, (6) can be integrated numerically with $F(R) = 2\mu(V_m(R) - E)$, as it can be deduced from (4). Both E and y must be obtained from the integration of the quasibound state potential, while for the dissociative state, E is given

and only y is sought. Since the Numerov method can not be applied to resonances, strictly speaking one should use its complex plane equivalent method developed by Atabek et al. [4]. However, since we are only interested in an order of magnitude estimate, we have opted for applying the Numerov method with a slight modification to the $2^2\Sigma_g^+$ potential to make it a bound one. This was done by replacing, from the top of the barrier, the downward tail of the potential with a straight line parallel to the R axis. The position of the resonance and the corresponding wavefunction are not expected to change much by this approximation. The R axis is now divided into a mesh of points with uniform interval ΔR , the size of which is determined by the desired accuracy. Once its size has been decided upon, ΔR must be kept constant throughout the calculation. Here, we have chosen $\Delta R = 4 \times 10^{-4}$ Bohr. The integration is initiated well inside the non-classical region where the wavefunction is zero for all practical purposes. The value of the first point, $y(0)$, is set to zero while the value of the second point, $y(\Delta R)$, is given an arbitrary small value, which is adjusted later by normalization. The third and subsequent values are obtained from Numerov's three point difference equation [3].

For the "bound" state, the method of Hajj [5] is used to compute E and y . This method eliminates the need for outward and inward integration by essentially pushing the matching point towards the end of the integration, where the value of the wavefunction is known to be zero. It requires an initial guess of E_0 , typically the value of the bottom of the well, and an initial decrement ΔE_0 , which is later varied at each iteration until the boundary condition at the chosen upper limit of integration, R_L , is fulfilled within an acceptable tolerance. A sequence of energies is thus obtained which eventually converges to the eigenvalue E . By increasing E_0 beyond E , the next eigenvalue can be found in the same way, and so on. Note that the corresponding eigenfunctions are not reliable beyond a point $R_M < R_L$. R_M is the point where the wavefunction "touches" the R axis for the last time for the selected root. R_L must be chosen so that it is slightly larger than R_M , but not by much. The normalization constant is determined by integrating y^2 from R_0 to R_M using either the trapezoidal or the Simpson rule. R_0 is the lower integration limit.

For the continuous state, one selects the previously determined eigenvalue E of the bound state in the computation of $F(R)$. The same R_0 , R_L , and ΔR as for

the bound state must be used. The integration is carried out as described by Blatt [3] except that ΔR is not varied. The continuous wavefunction χ_E must be energy normalized in order to be inserted in (3). This is done by fitting to the asymptotic form

$$\chi_E(R > R_M) = (2\mu/\pi k)^{1/2} kR [\cos \delta_l j_l(kR) - \sin \delta_l \eta_l(kR)], \quad (7)$$

where δ_l is the phase shift for orbital angular momentum l (here $l=0$), $k = (2\mu E)^{1/2}$ (in a.u.), j_l and η_l are the spherical Bessel and Hankel functions, respectively.

Finally, one must generate uniformly distributed points for $A(R)$, from the coefficients of its spline fit, at the same R 's as for $V_m(R)$. Then, χ_0 , χ_E and $A(R)$ are inserted in (3), which is integrated from R_0 to R_M employing either the trapezoidal or the Simpson rule. The implied differentiation of χ_0 in (3) is done point by point using the relation

$$\chi'_0(R_i) = [\chi_0(R_{i+1}) - \chi_0(R_i)]/\Delta R,$$

which is accurate enough for the chosen step size. If high accuracy is required, the method described in [3] should be used.

The resulting W is the transition rate $K_p(E)$. We have found that $K_p(E) \approx 0.49 \times 10^{15} \text{ sec}^{-1}$, which gives $\tau_p(E) \approx 0.2 \times 10^{-14} \text{ sec}$ and $\Gamma_p(E) \approx 2.619 \text{ cm}^{-1}$. This result is very close to that obtained by the Landau-Zener formula ($K_p(E) \approx 0.36 \times 10^{15} \text{ sec}^{-1}$) [6], and by a method based on the Stieltjes imaging theory ($K_p(E) \approx 0.42 \times 10^{15} \text{ sec}^{-1}$) [6]. Details of this last method have been published recently [7].

Conclusion

We have estimated the transition rate due to the vibronic interaction between the $1^2\Sigma_g^+$ and the $2^2\Sigma_g^+$ adiabatic states of He_2^+ to be of the order of 10^{15} sec^{-1} . This means that the probability of the system remaining in the $1\sigma_g 1\sigma_u^2$ diabatic state is very high, thus confirming, albeit to a limited extent, the well known strong diabaticity of the $2^2\Sigma_g^+$ excited states.

A consequence of this diabaticity, is that the adiabatic approximation is not very realistic for this particular system because the vibronic interaction is so strong that it may no longer be considered as a small perturbation. This point has been discussed by Dalgarno and his coworkers [8], who have also given details of the equivalent treatment via the diabatic approximation.

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- [1] T. F. O'Malley, *Adv. Atom. Mol. Phys.* **7**, 223 (1971).
- [2] A. Metropoulos, C. A. Nicolaides, and R. J. Buenker, *Chem. Phys.* **114**, 1 (1987).
- [3] J. M. Blatt, *J. Comp. Phys.* **1**, 382 (1967).
- [4] O. Atabek, R. Lefebvre, and A. Requena, *Mol. Phys.* **40**, 1107 (1980). – O. Atabek and R. Lefebvre, *Chem. Phys. Lett.* **84**, 233 (1981).
- [5] F. Y. Hajj, *J. Phys. B* **13**, 4521 (1980).
- [6] I. D. Petsalakis, unpublished results.
- [7] I. D. Petsalakis, G. Theodorakopoulos, and R. J. Buenker, *Phys. Rev. A* **38**, 4004 (1988).
- [8] E. F. van Dishoeck, M. van Hemert, A. C. Allison, and A. Dalgarno, *J. Chem. Phys.* **81**, 5709 (1984).