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Errors in the application of the JWKB method to calculating the survival factor in dissociative electron attachment using the local complex potential

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The accuracy of the JWKB method for determining the survival factor defined for dissociative electron attachment (DEA) processes is examined for a range of electronic resonance lifetimes within the local complex potential approximation. The author concludes that the accuracy is inadequate for molecules with properties commonly found for shape resonance induced DEA. More accurate methods using the uniform Airy function approximation give much better results, but the direct numerical integration of Schrödinger's equation appears simpler still. © 2007 American Institute of Physics. [DOI: 10.1063/1.2434977]

I. INTRODUCTION

Over 50 years ago Holstein,¹ described dissociative electron attachment (DEA) as a two step process governed by the Franck-Condon principal and the Born-Oppenheimer approximation,



With this picture the expected total cross section is the product of the capture cross section for the electron to form an autodetaching (temporary) negative ion and the survival factor (SF), the probability that the A–B distance increase to the point where the B[−] ion is stable. Thus he wrote the cross section as

$$\sigma_{\text{DEA}} = \sigma_{\text{cap}} \exp(-\Gamma\tau/\hbar),$$

where \hbar/Γ is the lifetime of the ion, and τ is the time required for the ion to reach the geometry of stability.

In the next 30-odd years other studies of DEA appeared.^{2–6} Many of these assumed that the nuclear motion proceeds under the influence of a local (multiplicative) complex potential operator and also used the JWKB method to approximate the wave functions. These studies all arrived at essentially equivalent results, and found that the SF, which we symbolize as P_{DEA} , may be written as

$$P_{\text{DEA}} = e^{-\rho}, \quad (1)$$

$$\rho = \frac{2}{\hbar} \text{Im} \left[\int_{R_0'}^{R_c} \sqrt{2\mu[E_{\text{ion}} - V_{\text{ion}} + i\Gamma/2]} dR \right]. \quad (2)$$

Figure 1 shows a schematic version of the parts of the complex nuclear potential energy function in Eq. (2), as well as the potential for the neutral molecule and a horizontal line indicating the asymptotic energy of the ion and neutral fragments. Figure 1 also shows the special value, R_c , the point where the real part of the ion curve crosses the neutral curve. For $R > R_c$ the ion is stable.

The other integral limit in Eq. (2), R_0' , is a complex function of E_{ion} and cannot be included in the figure as a point on the real R axis. We return to this quantity later.

Equation (2) merely gives the imaginary part of the asymptotic JWKB phase integral, which, as we shall see, provides the SF in that approximation.

In the early discussions it was also customary to make further approximations in order to cast the results in a form closer to that originally given by Holstein. Under certain circumstances the square root in Eq. (2) may be approximated so that one obtains

$$\rho = q + \frac{1}{\hbar} \int_{R_0}^{R_c} \frac{\Gamma(R) dR}{v(R)}, \quad (3)$$

and R_0 is defined by

$$E_{\text{ion}} - V_{\text{ion}}(R_0) = 0. \quad (4)$$

In Eq. (3) $v(R)$ is the classical velocity of dissociation and q is a real constant that results from the $R_0' \rightarrow R_0$ part of the

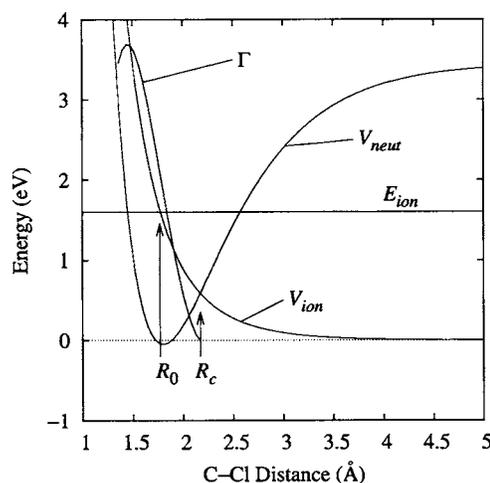


FIG. 1. Schematic neutral molecule and ion potential curves for a pseudodiatom similar to CF_3Cl . The symbols marking various points are described in the text.

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integral in Eq. (2). Thus, the second term, at least, on the right of Eq. (3) resembles the Holstein result.

The previous studies also all make statements to the effect that Eqs. (2) and (3) are valid if $\Gamma(R)$ is small enough. Although this is certainly true at some level, quantitative estimates of the limits of this validity apparently have never been published. The primary purpose of the present article is to examine this question in detail and rectify the omission.

We first give a careful definition of the local complex potential (LCP), we then examine the solution of Schrödinger's equation for the semiclassical approximation, examining the errors, and then compare these results with an accurate numerical integration of the differential equation.

II. THE LOCAL COMPLEX POTENTIAL

We will be discussing the application of semiclassical methods to the problem of calculating the SF, and it is well known that these asymptotic procedures can depend crucially upon the analyticity of the terms in Schrödinger's equation being treated. We must therefore define the LCP carefully before we begin our discussion. The pieces of this potential have already been illustrated in Fig. 1, but we explain further details here.

The two potentials $V_{\text{neut}}(R)$ and $V_{\text{ion}}(R)$ are real functions of a real R , and we assume that they have analytic continuations into the whole complex R plane. For any computations done in this article, we assume that they are represented by some form of Morse function, which will satisfy the requirement. Finally, we define the energy difference $d(R) = V_{\text{ion}}(R) - V_{\text{neut}}(R)$, which is also analytic everywhere in the R plane.

The point, R_c , on the real R axis where $V_{\text{neut}}(R_c) = V_{\text{ion}}(R_c)$ is important and divides the real R space into two regions **T** and **S**. **T** is composed of the points $R < R_c$ and is the region where the negative ion is temporary and autodetaching. **S** is the region where $R > R_c$ and the ion is stable.

In region **T** where the ion is autodetaching, we write the complete LCP as

$$W(R) = V_{\text{ion}} - \frac{i}{2}\Gamma(R), \quad R < R_c, \quad (5)$$

where

$$\Gamma(R) = \text{const} \times d(R)^m, \quad (6)$$

and we assume for the purposes of this article that m is a rational number. In region **S** where the ion is stable we assume

$$W(R) = V_{\text{ion}}(R), \quad R > R_c. \quad (7)$$

Thus, since $d(R_c) = 0$, $W(R)$ is continuous on real R , and depending upon the value of m , possibly even smooth.

Nevertheless, $W(R)$ is not analytic everywhere, since its analytic continuation from the **T** region is not the same as that from the **S** region. Thus, treating Schrödinger's equation with this potential using the JWKB procedure requires one to make a careful analysis of the possible impact of this fact.

The derivation of this form for the LCP approximation has been given by a number of workers,^{2,3,7} and we shall use it in succeeding sections.

III. THE INHOMOGENEOUS SCHRÖDINGER EQUATION, THE CAPTURE CROSS SECTION, AND THE SURVIVAL FACTOR

Schrödinger's equation containing the LCP for nuclear motion has been given by a number of workers,^{2,3,7} and the result takes the form

$$[K - E + W(R)]\xi^{(i)}(R) = v_{ik}(R)\zeta_v, \quad (8)$$

where the superscript (i) denotes the solution of the inhomogeneous equation, K is the nuclear kinetic energy operator,

$$-\frac{1}{2\mu} \frac{d^2}{dR^2},$$

ζ_v is the vibrational wave function of the neutral molecule, and we are using a.u. throughout. Once Eq. (8) is solved the DEA cross section is determined from⁸

$$\sigma_{\text{DEA}} = \lim_{R \rightarrow \infty} \frac{2\pi^2 K_a}{k_e^2 \mu} |\xi^{(i)}(R)|^2, \quad (9)$$

where k_e is the incident electron momentum. Equation (8) is more conveniently written in the form

$$\frac{d^2 \xi^{(i)}}{dR^2} + 2\mu[E - W(R)]\xi^{(i)} = -2\mu v_{ik}(R)\zeta_v, \quad (10)$$

where $v_{ik}(R)$ is frequently approximated by $\sqrt{\Gamma(R)/(2\pi)}$. In some applications it is appropriate to include a power of $d(R)$ in $v_{ik}(R)$ as a factor.⁹

Equation (10) is most conveniently solved using Green's function, which we write as

$$G(R, R') = \chi^{\text{reg}}(R_<) \chi^{\text{irreg}}(R_>)/K_a, \quad (11)$$

where

$$\lim_{R \rightarrow \infty} \chi^{\text{reg}}(R) = \sin(K_a R + \delta), \quad (12)$$

$$\lim_{R \rightarrow \infty} \chi^{\text{irreg}}(R) = \exp(iK_a R + i\delta), \quad (13)$$

$$K_a = \lim_{R \rightarrow \infty} \sqrt{2\mu[E - W(R)]}, \quad (14)$$

and

$$\rho/2 = \text{Im}(\delta). \quad (15)$$

Assembling these pieces and using Eq. (9), we see that

$$\lim_{R \rightarrow \infty} \xi^{(i)} = -2\mu \langle \chi^{\text{reg}} | v_{ik} | \zeta_v \rangle \exp(iK_a R + i\delta)/K_a, \quad (16)$$

and therefore

$$\sigma_{\text{DEA}} = \frac{8\pi^2 \mu}{K_a k_e^2} |\langle \chi^{\text{reg}} | v_{ik} | \zeta_v \rangle|^2 \exp(-\rho). \quad (17)$$

It is conventional⁵ to consider the final factor on the right of Eq. (17), $\exp(-\rho)$, the entirety of the SF, and the remaining part the capture cross section. This is not an entirely rigorous

suggestion, since we see that the matrix element in Eq. (17) also depends upon ρ . Nevertheless, for low values of v the Franck-Condon region implied by ζ_v is so narrow that the integral will not probe regions of larger R where χ^{reg} has grown large, because this will not happen well within region **T**. Clearly, we could consider this factorization to become meaningless for large v .

On the other hand, one could arbitrarily define the SF as above and assume the position that the capture cross section simply grows with increasing v to offset the effects of the SF. The alternatives seem mainly a matter of taste.

Writing the regular solution of the homogeneous equation in a different way so that its asymptotic form is

$$\chi^{\text{reg}} \rightarrow S \exp(iK_a R) - \exp(-iK_a R), \quad (18)$$

one can show that the absolute value of the scattering matrix, $S = e^{2i\delta}$, is the SF,

$$e^{-\rho} = |S|. \quad (19)$$

It should be pointed out that the process reverse to DEA, associative electron detachment (AED), has the square of this SF as the decay in the elastic channel in atom-ion collisions. We do not discuss this further, however.

We now work out the semiclassical solutions of the homogeneous version of Eq. (10),

$$\frac{d^2 \chi^{\text{reg}}}{dR^2} + 2\mu[E - W(R)]\chi^{\text{reg}} = 0, \quad (20)$$

and investigate their accuracy. As will be seen, a complete analytic answer to the accuracy problem is likely to be very difficult to obtain, but some analytic results are available, and along with these we compare the semiclassical solutions and accurate numerical solution of Eq. (20) using different potential functions with varying parameters.

IV. THE JWKB FUNCTIONS

The JWKB method has a long history, but has been discussed in detail most recently by Heading,¹⁰ Fröman and Fröman,¹¹⁻¹³ and Maslov.¹⁴ As discussed in Sec. II, we have a potential with two different regions of analyticity, and we need a JWKB solution valid in each of them and splice these together on either side of the boundary point R_c .

Region T. The classical turning point (CTP) in this region is R'_0 referred to in Eq. (2) in Sec. I. It is the solution to the equation

$$E - W(R'_0) = 0. \quad (21)$$

The JWKB function valid in the classically allowed region (CAR) and exponentially decreasing for small R is

$$\phi_T = \frac{1}{\sqrt{p(R)}} \cos\left(\int_{R'_0}^R p dR - \frac{\pi}{4}\right), \quad (22)$$

if the upper limit on the integral, R , is not too close to the CTP, and where

$$p(R) = \sqrt{2\mu[E - W(R)]}. \quad (23)$$

Region S. The CTP in this region is R_0 the solution to Eq. (4) in Sec. I. In this case we need both of the solutions

valid in the CAR, which are similar to ϕ_T except with both the sine and the cosine. Because of the simple properties of the trigonometric functions, we may match the functions from the two regions with a phase change, and therefore

$$\phi_S = \frac{1}{\sqrt{p(R)}} \cos\left(\int_{R_0}^R p dR - \frac{\pi}{4} + \theta\right), \quad (24)$$

if the upper limit on the integral, R , is again not too close to the CTP. Setting $\phi_T(R_c) = \phi_S(R_c)$, we see that the correct function for region **S** is

$$\phi_S = \frac{1}{\sqrt{p(R)}} \cos\left(\int_{R'_0}^R p dR - \frac{\pi}{4}\right). \quad (25)$$

A little algebra shows that in Eq. (3) the quantity $q = 2 \text{Im}(\theta)$.

Thus the result of Eq. (2) is confirmed, so long as $|R_c - R'_0|$ and $|R_c - R_0|$ are both large enough.

Some further progress in making this quantitative is possible using an error estimate given by Kemble.¹⁵ If one determines the exact differential equation satisfied by ϕ_S , it is found to be

$$\phi_S'' + [2\mu(E - V) - Q]\phi_S = 0, \quad (26)$$

$$Q = \frac{5}{16} \left(\frac{V'}{E - V}\right)^2 + \frac{1}{4} \frac{V''}{E - V}, \quad (27)$$

and, if

$$\left| \frac{Q}{2\mu(E - V)} \right| \ll 1, \quad (28)$$

the JWKB function is a good approximation to the correct wave function. In Sec. VI we will use DEA in CF_3Cl as an example to make further tests of the accuracy of the semiclassical approach numerically, but using data for that system we find that

$$\left| \frac{Q}{2\mu(E - V)} \right| \approx 10^{-3},$$

at the energy of the electronic resonance. It will be observed, however, that the error quantity is $\propto (E - V)^{-3}$ and will increase very rapidly as the energy goes lower to the region of the DEA peak. The error blows up at the energy of the crossing point.

V. THE UNIFORM AIRY FUNCTION APPROXIMATION

In Sec. IV we examined the behavior of the LCP with the JWKB solutions, which are valid only in the asymptotic region. Since for some energies R_c is not in the asymptotic region, an alternative treatment is called for. This is available using the uniform Airy function approximation (UAFA), which is valid up to and through the CTP, as well as in the asymptotic region. This sort of approximate solution has been discussed, in particular, by Heading,¹⁰ and for the present purposes we need

$$\phi_T(R) = \frac{\Pi_T^{1/6}}{\sqrt{p}} \text{Ai}(-\Pi_T^{2/3}), \quad (29)$$

TABLE I. Data for CF₃Cl.

C-Cl bond dissociation energy	3.76 Å
Equilibrium bond distance in neutral	1.76 Å
Temporary negative ion energy	1.85 Å
Equilibrium <i>R</i> resonance width	1.83 Å

$$\phi_S(R) = \frac{\Pi_S^{1/6}}{\sqrt{p}} [A \text{Ai}(-\Pi_S^{2/3}) + B \text{Bi}(-\Pi_S^{2/3})], \quad (30)$$

where

$$\Pi_T(R) = \frac{3}{2} \int_{R'_0}^R p(R') dR', \quad (31)$$

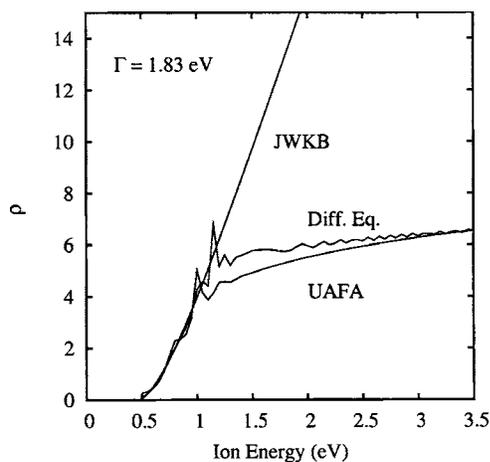
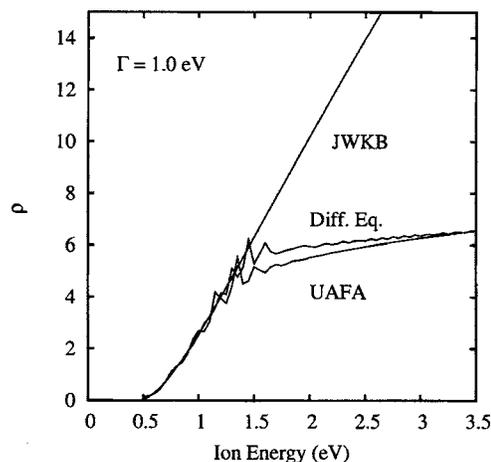
$$\Pi_S(R) = \frac{3}{2} \int_{R_0}^R p(R') dR', \quad (32)$$

as before. In Eq. (30) *A* and *B* are determined by equating $\phi_T(R_c)$ and $\phi_S(R_c)$, and also the derivatives. The result in this case is not so simple as that with the JWKB functions, and in general, we do not arrive at an expression with a single phase integral expression integrated from R'_0 to ∞ . In this case, therefore, we examine the results numerically, comparing the SF determined with JWKB functions, the UAFA, and a high precision numerical integration of Schrödinger's equation.

VI. A NUMERICAL COMPARISON OF THREE METHODS OF CALCULATION

DEA has been measured for CF₃Cl by Aflatooni and Burrow¹⁶ and Hahndorf *et al.*¹⁷ The latter workers devised a set of parameters for use in connection with their studies, and we use these for our numerical comparison. Some of the parameters are shown in Table I. In addition to the values shown in the table, Hahndorf *et al.* determine further parameters that represent the potential functions in terms of Morse functions, which are similar to what is shown in Fig. 1.

In order to assess the errors in the direct phase integral treatment, we show the quantity ρ in Figs. 2–5 for varying values of $\Gamma(R_{\text{eq}})$. These are 1.83, the value corresponding to experiment, and then values artificially reduced to 1.0, 0.5,

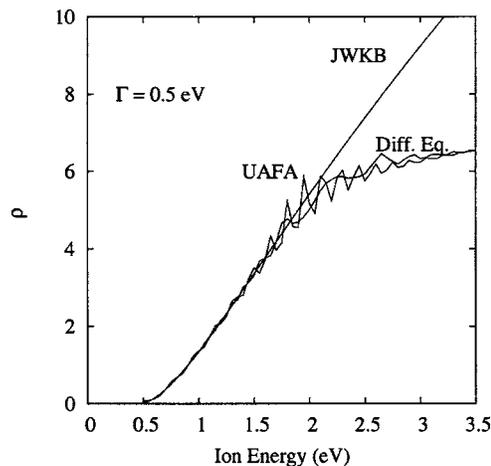
FIG. 2. Comparison of three methods for $\Gamma(R_{\text{eq}})=1.83$ eV.FIG. 3. Comparison of three methods for $\Gamma(R_{\text{eq}})=1.0$ eV.

and 0.1, all in eV. Each of these figures shows ρ calculated with the JWKB functions, with the UAFA, and using a conventional Bulirsch-Stör¹⁸ numerical integration of the differential equation, which we assume to be the “correct” answer for the LCP. In all cases the three methods give nearly the same results with increasing energy for values of ρ up to around 4. Thereafter, the simple phase integral result continues in a roughly straight line, while the other procedures give qualitatively similar results with considerable structure. Since even the UAFA treatment is expected to be more approximate than the numerical integration, the latter two results are not identical.

The shape resonance in CF₃Cl is in the neighborhood of 1.8 eV, and the crucial point shown in Fig. 2 is that the traditional phase integral result for ρ is off by a value of roughly 6 in that region. This corresponds to an error factor of $\approx 2 \times 10^{-3}$ in the SF. As $\Gamma(R_{\text{eq}})$ decreases, the error in the vicinity of the resonance becomes smaller in the manner predicted, but one must have a Γ as low as 0.1 eV for all methods to give substantially the same result.

VII. DISCUSSION

The results in the last section clearly show that the simple JWKB phase integral expression for ρ is inadequate

FIG. 4. Comparison of three methods for $\Gamma(R_{\text{eq}})=0.5$ eV.

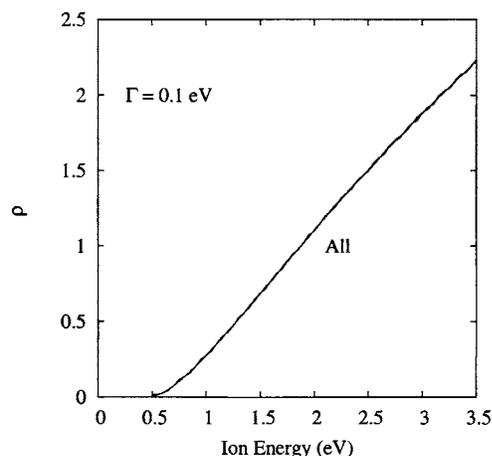


FIG. 5. Comparison of three methods for $\Gamma(R_{eq})=0.1$ eV.

for Γ values in the typical ranges seen for shape resonances, and it appears that the JWKB function approach overestimates to a considerable extent the decay of the negative ion while DEA is occurring. This is equally true, of course, when considering the reverse process, AED. Values of Γ around 0.1 eV might be expected for core excited or Feshbach resonances that could lead to DEA, and for these the JWKB result is more likely to be adequate.

The UAFA semiclassical method is clearly much more accurate, but, nevertheless, the semiclassical method in any form can hardly be recommended in today's computational environment for a problem like that of determining the SF. Direct numerical integration of one dimensional Schrödinger's equation is so routine and so much simpler than the semiclassical method, where considerable attention to all of the complicated branch points and Stokes regions is required. The fairly large number of calculations of DEA in the literature also attests to this conclusion.

The undulatory structure seen in ρ at higher energies is a result of the complex nature of the LCP. A reader can easily convince oneself of this by examining the SF for a simple complex square well potential in s -wave approximation. For DEA it seems not very interesting, since it appears to occur only in energy regions where cross sections are likely to be too small to be observed and, in addition, the effect might be obscured by variations in the capture cross section.

However, all of these observations and conclusions depend upon an assumption we have not discussed, viz., that concerning the adequacy of the LCP approximation in the first place. As noted by O'Malley¹⁹ and discussed in detail by Domcke,²⁰ the actual potential function governing nuclear motion during molecular electronic resonances is nonlocal and nonadiabatic and only approximately represented by the LCP. Nevertheless, the latter form appears to have a useful role in understanding systematic trends in series of similar molecules (see Ref. 7). It would therefore be doubly interesting if the SF undulations noted above should ever be observed in a propitious case.

ACKNOWLEDGMENT

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