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Collisional Ionization as a Nonlocalized Process and the Breakdown of the Franck–Condon Approximation

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It is demonstrated by a model computation based on a semiclassical theory that in collisional ionization the Franck–Condon approximation, equivalent to the assumption that the ionization event takes place locally, does not always apply.

I. Introduction

We consider collisional ionization processes of the type

$$A^* + B \rightarrow A + B^+ + e^-$$

usually referred to as Penning ionization.[1] The conceptual picture most often used in the description of such processes hinges on the Franck–Condon (FC) or quasistatic approximation: namely, an electron of energy ϵ can only be emitted at the particular internuclear distance R where

$$\epsilon = W_2(R) - W_1(R) \tag{1}$$

$W_2(R)$ and $W_1(R)$ being the potential energy curves correlating to $A^* + B$ and $A + B^+$, respectively. This picture of localized transitions, while intuitively appealing and generally useful, has never been directly verified. Indeed, many previous approaches[2-9] to the problem of Penning ionization have preferred to adopt it as the starting point of their formulations. In this work we report on a model computation based on the He + Ar system which demonstrates explicitly the failure of the localized-transitions picture. Although this example by no means rules out the validity of the FC approximation in many cases,[10] certain doubts can now be raised about its indiscriminate use.

It is perhaps useful to recall the origin of the FC approximation. The crucial point is that, for a system involving bound-continuum interactions, the Schrödinger equation does not lead to a differential equation but to a differential–integral equation of the form[6] (ignoring the complications due to partial-wave decomposition)

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + W_2(R) - E\right)\psi_2(E,R) = I \tag{2}$$

where

$$I \propto \int d\epsilon \int dR'\, V_\epsilon^*(R)\, V_\epsilon(R')\, \rho(\epsilon)\, \psi_1(E_0',R) \times \psi_1(E_0',R')\, \psi_2(E,R') \tag{3}$$

$$E_0' = E - \epsilon \tag{4}$$

and $V_\epsilon(R)$ represents the bound-continuum coupling parametrized by the electronic energy ϵ (defined in eq 5). Equation 3 clearly indicates the nonlocality of the potential. This potential, however, can be localized with the help of the FC approximation.[6] It consists of the following: in the integration over ϵ in eq 3, only those values of ϵ are considered important for the R' integration at which the product $\psi_1(E_0',R')\, \psi_2(E,R')$ is slowly varying. If the wave functions $\psi_{1,2}$ are regarded as WKB wave functions, and also if $V_\epsilon(R)$ is assumed to be slowly varying, the stationary-phase approximation, together with eq 4, would immediately lead to the FC resonance condition eq 1. Thus, in the ϵ integral, ϵ can be regarded as a function of R (given by eq 1) in the product $V_\epsilon^*(R)\, V_\epsilon(R')$. By virtue of the completeness of the set $\{\psi_1(E,R)\}$ the rest of the ϵ integral leads to the delta function $\delta(R - R')$ and localization is finally achieved through the R' integration. It therefore appears that any theory which employs a width factor $\Gamma_\epsilon(R) = \pi\rho(\epsilon)|V_\epsilon|^2$ in a complex potential has already implicitly (or explicitly) made use of the FC approximation: in that a differential–integral equation (involving a nonlocal potential) has been reduced to a differential equation (involving only a local, though complex, potential).

Our approach is to avoid using the basis set of the electronic Hamiltonian (H_{el}) leading to eq 2 and thus bypass using the FC approximation for localization at this early stage. Instead, a basis set consisting of eigenfunctions of H_{el} (the adiabatic representation) is chosen, with the result that a simpler equation consisting of nonlocality only for ϵ (eq 24) is obtained. This equation is simpler in the sense that the kernel $K(\epsilon,\epsilon')$ is of a very favorable nature: it is separable. We have shown previously[11] that this important feature allows eq 24 to be recast in the form of an integral equation of a relatively simple type, thus permitting a solution without introducing any localization approximation a priori. Interesting as it is, we will, however, not pursue this path here. Our rationale in this work is the following: having established a formalism in which a localization approximation is not incorporated in the first place, we have the option of carrying it through with or without making that approximation at some later stage, and make a comparison. This will be done via a perturbative solution of eq 24. Our purpose, then, is to investigate whether a localization condition (either of the form of eq 1 or of some other general form $\epsilon = \epsilon(R)$) will suffice for the solution of eq 24.

Our computation is based on a general semiclassical theory of collisional ionization developed earlier,[11] which treats explicitly the nonlocalization of the transitions between W_2 and W_1. In section II, the relevant parts of this theory will be briefly reviewed (more complete derivations

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(1) For a review of this subject, see A. Niehaus in "Advances in Chemical Physics", Vol. 45, Part 2, J. Wm. McGowan, Ed., Wiley, New York, 1981, p 399 ff.

(2) T. F. O'Malley, *Phys. Rev.*, 150, 14 (1966).

(3) M. Mori, *J. Phys. Soc. Jpn.*, 26, 773 (1969).

(4) H. Nakamura, *J. Phys. Soc. Jpn.*, 26, 1473 (1969).

(5) W. H. Miller, *J. Chem. Phys.*, 52, 3563 (1970).

(6) R. J. Bieniek, *Phys. Rev. A*, 18, 392 (1978).

(7) J. C. Bellum and D. A. Micha, *Phys. Rev. A*, 18, 1435 (1978).

(8) K.-S. Lam, J. C. Bellum, and T. F. George, *Chem. Phys.*, 33, 219 (1978).

(9) J. S. Dahler, R. E. Turner, and S. E. Nielsen, *J. Phys. Chem.*, 86, 1065 (1982).

(10) L. R. Relyea and D. A. Micha, *Int. J. Quantum Chem., Quantum Chem. Symp.*, 13, 569 (1979). In this work, the validity of the Franck–Condon approximation for total ionization cross sections (summed over all the partial waves and integrated over ϵ) is demonstrated indirectly through the use of the two-state approximation within a discretized multichannel formalism. In our work, we attempt to investigate the Franck–Condon approximation at the more basic level of single partial waves and ϵ.

(11) K.-S. Lam, T. F. George, and D. K. Bhattacharyya, *Phys. Rev. A*, 27, 1353 (1983).

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of equations presented therein can be found in ref 11). Section III will deal with the model computation and its results; and finally, in section IV, we will discuss some pertinent problems for future investigations.

II. Theory

A diabatic basis set $\{|\phi_2(t)\rangle, |\Phi_+(t),\epsilon\rangle\}$ corresponding to W_2 and W_1 are assumed such that the following conditions are satisfied:

$$\langle\phi_2(t)|H|\phi_+(t),\epsilon\rangle = V_\epsilon(t) \tag{5}$$

$$\langle\phi_+(t),\epsilon|H|\phi_+(t),\epsilon'\rangle = (W_1(t) + \epsilon)\delta_{\epsilon\epsilon'} \tag{6}$$

$$\langle\phi_2(t)|H|\phi_2(t)\rangle = W_2(t) \tag{7}$$

$$\langle\phi_2|\dot\phi_2\rangle = \langle\phi_{+,\epsilon}|\dot\phi_{+,\epsilon'}\rangle = 0 \tag{8}$$

$$\langle\phi_2|\dot\phi_{+,\epsilon}\rangle = \langle\dot\phi_2|\phi_{+,\epsilon}\rangle = 0 \tag{9}$$

with H being the total Hamiltonian involving electronic coordinates. Equation 5 defines the bound-continuum configuration-interaction coupling $V_\epsilon(t)$, while eq 6 implies that there are no couplings between the different continuum states. (The quantization volume of the system will eventually be allowed to approach infinity so that the discrete indices will become continuum ones.) Equations 8 and 9 specify the condition of the absence of "velocity" or nonadiabatic couplings.

As discussed in ref 11, eq 5–9 are simply taken to constitute the "model" of the present theory, and questions concerning the explicit construction of the diabatic states or even their existence will not be dealt with here. The present theory also makes use of classical trajectories for the A–B relative motion (with internuclear coordinate trajectory $R(t)$), so that V_ϵ, W_2, and W_1 all become explicit functions of time, as they appear in eq 5–7.

We now choose an adiabatic representation $\{|\phi_\epsilon(t)\rangle\}$ in which nonadiabatic couplings do not vanish, but which comprise the exact eigenstates of H:

$$H|\phi_\epsilon(t)\rangle = (W_1 + \epsilon)|\phi_\epsilon(t)\rangle \tag{10}$$

These can be expanded in terms of the diabatic set:

$$|\phi_\epsilon(t)\rangle = \beta_\epsilon(t)|\phi_2(t)\rangle + |\phi_+(t),\epsilon\rangle + \sum_{\epsilon'}\chi_{\epsilon\epsilon'}(t)|\phi_+(t),\epsilon'\rangle \tag{11}$$

It can then readily be deduced that

$$\chi_{\epsilon\epsilon'}(t) = \frac{-\beta_\epsilon(t)\, V_{\epsilon'}^*(t)}{\epsilon' - \epsilon - i0^+} \tag{12}$$

$$\beta_\epsilon(t) \simeq \frac{-V_\epsilon}{W_{21}(t) - \epsilon - i\Gamma_\epsilon(t)} \tag{13}$$

with the instantaneous level width given by

$$\Gamma_\epsilon(t) \equiv \pi\rho(\epsilon)|V_\epsilon|^2 \tag{14}$$

where $\rho(\epsilon)$ is the energy density of continuum states and $W_{21} \equiv W_2 - W_1$.

Now $|\phi_\epsilon(t)\rangle$ represents Franck–Condon "stationary" states, so that "wave packets" including the effects of nonadiabatic transitions between the $|\phi_\epsilon(t)\rangle$ can be constructed:

$$|\psi(t)\rangle = \sum_\epsilon \gamma_\epsilon(t)\exp\left\{-(i/\hbar)\int_0^t dt'\,[W_1(t') + \epsilon]\right\}|\phi_\epsilon(t)\rangle \tag{15}$$

The time-dependent Schrödinger equation then yields the equation of motion for $\gamma_\epsilon(t)$:

$$\dot\gamma_\epsilon = -\sum_{\epsilon'}\gamma_{\epsilon'}\langle\phi_\epsilon|\dot\phi_{\epsilon'}\rangle e^{(i/\hbar)(\epsilon'-\epsilon)t} \tag{16}$$

The initial condition is given by

$$|\psi(0)\rangle = |\phi_2(0)\rangle \tag{17}$$

which implies

$$\gamma_\epsilon(0) = \beta_\epsilon^*(0) \tag{18}$$

The transition probability for the ionization process is given by

$$\lim_{t\to\infty}|S_\epsilon(t)|^2$$

where

$$S_\epsilon(t) \equiv \langle\phi_+(t),\epsilon|\psi(t)\rangle \tag{19}$$

This quantity can be expressed in terms of the time-dependent coefficients $\gamma_\epsilon(t)$ as[11]

$$|S_\epsilon(t)|^2 \simeq |\gamma_\epsilon(t)|^2\left[1 + \frac{3\Gamma_\epsilon^2(t)}{(W_{21}(t) - \epsilon)^2 + \Gamma_\epsilon^2(t)}\right] \tag{20}$$

There is one such quantity $S_\epsilon^{(L)}$ for each partial wave characterized by the orbital angular momentum quantum number L of the A–B relative motion. The total differential ionization cross section (with respect to electronic energy ϵ), $d\sigma/d\epsilon$, is then given by

$$d\sigma/d\epsilon = (\pi\rho_\epsilon/K_0^2)\sum_L(2L + 1)|S_\epsilon^{(L)}|^2 \tag{21}$$

where

$$K_0^2 = 2\mu E_t/\hbar^2 \tag{22}$$

with μ being the reduced mass and E_t the total collision energy of the system.

If we now make the assumption that the time variation of Γ_ϵ is insignificant, i.e.

$$|\dot\Gamma_\epsilon| \ll |\dot W_{21}| \tag{23}$$

Equation 16, on passing to the continuum limit in the energy variable ϵ', can be shown[11] to be equivalent to the following differential–integral equation for γ_ϵ:

$$\dot\gamma_\epsilon + \frac{i\Gamma_\epsilon\dot W_{21}}{(W_{21} - \epsilon - i\Gamma_\epsilon)^2}\gamma_\epsilon = \frac{\dot W_{21}V_\epsilon^*}{(W_{21} - \epsilon + i\Gamma_\epsilon)}\int_0^\infty d\epsilon'\,\frac{\rho_{\epsilon'}V_{\epsilon'}\gamma_{\epsilon'}e^{-(i/\hbar)(\epsilon'-\epsilon)t}}{(W_{21} - \epsilon' - i\Gamma_{\epsilon'})^2} \tag{24}$$

We note that the separability of the kernel in the above equation permits it to be recast as an integral equation—a Volterra equation of the second kind.[11] We will here, however, pursue a perturbative solution based on the assumption

$$\gamma_{\epsilon'}(t) \sim \beta_{\epsilon'}^*(t) \tag{25}$$

which is to be used in the right-hand side of eq 24. Since $\beta_\epsilon(t)$ is a known quantity (eq 13), eq 24 reduces to a first-order ordinary differential equation. Provided that for the collision times t of interest

$$t \ll \hbar/2\Gamma_\epsilon \tag{26}$$

the solution to this differential equation is given approximately by[11]

$$\gamma_\epsilon(t) \simeq \gamma_\epsilon(0) + \frac{i}{2(\pi\rho_\epsilon)^{1/2}}\int_0^t dt'\,\frac{\dot W_{21}e^{(i/\hbar)(\epsilon - W_{21})t'}e^{-t'\Gamma_\epsilon/\hbar}}{\Gamma_\epsilon^{1/2}(\epsilon - W_{21} - i\Gamma_\epsilon)} \tag{27}$$

The integral is of a form such that the stationary-phase approximation is likely to be applicable for its evaluation. This approximation would be exact in the strict classical limit $\hbar \to 0$; and in a great variety of collision problems

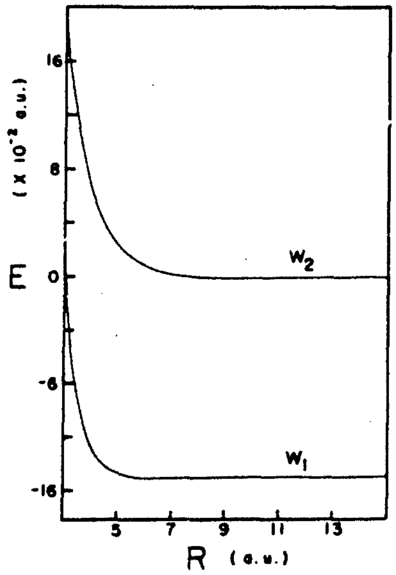

Figure 1. Potential curves for the He + Ar collisional ionization system. $W_2(R)$ correlates to He*(1s2s,^{3}S) + Ar and $W_1(R)$ to He + Ar$^+$. All quantities are in atomic units.

treated in the semiclassical context which do not involve bound-continuum interactions, it is indeed found to be excellent.[12] The advantage of the stationary-phase approximation, when valid, is that the result allows a very interesting physical interpretation of the collision process, namely, transitions take place *locally* in configuration space. In the context of eq 27, the lowest order stationary-phase result would be given by

$$\gamma_\epsilon^{\mathrm{sp}}(t) \simeq \gamma_\epsilon(0) + \frac{i}{2(\pi\rho_\epsilon)^{1/2}} \sum \left(\left(\frac{2\hbar\pi}{|2\dot{W}_{21}(t_0) + \ddot{W}_{21}(t_0)t_0|} \right)^{1/2} \times \frac{e^{-t_0\Gamma_\epsilon(t_0)/\hbar}}{(\Gamma_\epsilon(t_0))^{1/2}\left(t_0 - \frac{i\Gamma_\epsilon(t_0)}{\dot{W}_{21}(t_0)} \right)} \exp\left\{ \frac{i}{\hbar} \dot{W}_{21}(t_0) t_0^2 \right\} e^{\pm i\pi/4} \right) \quad (28)$$

In this equation the sum is over the stationary points t_0 which satisfy

$$\epsilon - W_{21}(t) = \dot{W}_{21}(t)t \quad (29)$$

the ± signs in the exponential are to be used according as $-2\dot{W}_{21} - \ddot{W}_{21}t > \text{or} < 0$. If eq 28 is valid, the most important contributions to the ionization process would then be *localized* to the discrete times t_0, or the discrete configurations $R(t_0)$, where R is the A-B internuclear coordinate. The fact that there may be more than one stationary point for a particular trajectory leads to quantum interference effects within a semiclassical treatment.

We recall that in most conventional interpretations of Penning ionization, localization, according to the Franck-Condon approximation (eq 1), is assumed to take place where

$$\epsilon - W_{21}(t) = 0 \quad (30)$$

Equation 29, however, indicates that, when localization applies at all, it takes place at points quite different from those implied by eq 30. In fact, since $\dot{W}_{21}$ has opposite signs on the incoming and outgoing portions of the trajectory, the "true" stationary configurations ($R(t_0)$) may be shifted to either side of the Franck-Condon configurations by an appreciable amount.

At this point, we have no a priori reason to expect that the stationary-phase approximation will work for eq 27. Indeed, it may be surmised that, since the present problem involves bound-continuum interactions, localization, whether it conforms to the Franck-Condon points or not, would *not* be expected to take place. In the next section we will attempt to settle the question by performing calculations on a specific model system.

III. Model System and Results

We apply eq 27 to the He*(1s2s,^{3}S) + Ar Penning ionization system using the following model potential curves (all values are given in atomic units):[8]

$$W_2(R) = V_2(R) \quad (31a)$$

$$W_1(R) = V_1(R) - E_0 \qquad E_0 = 0.149 \quad (31b)$$

$$V_i(R) = A_i e^{-R/b_i} - \theta_i(R)\,\phi_i(R) \qquad i = 1, 2 \quad (32)$$

$$\theta_i(R) = C_{6i}/R^6 + C_{4i}/R^4 \quad (33)$$

$$\phi_i(R) = [1 + \exp\{-(R - R_{0i})/b_i\}]^{-1}[1 + \beta_i\{1 + \exp[(R - R_{0i})/b_i]\}^{-1}] \quad (34)$$

$$A_1 = 44.65270 \qquad A_2 = 4.39678 \quad (35)$$

$$b_1 = 0.5310 \qquad b_2 = 0.9675 \quad (36)$$

$$C_{61} = 7.94 \qquad C_{62} = 226.0 \quad (37)$$

$$C_{41} = 0.6904 \qquad C_{42} = 0.0 \quad (38)$$

$$\beta_1 = 6.42317 \qquad \beta_2 = 2.81505 \quad (39)$$

$$R_{01} = 5.76899 \qquad R_{02} = 8.73010 \quad (40)$$

These potential curves are shown in Figure 1 (drawn to scale). The interaction configuration coupling strength Γ_ϵ is taken to have a constant value:

$$\Gamma_\epsilon = 1.056 \times 10^{-5} \quad (41)$$

This assumption of constant coupling strength may be somewhat unrealistic as Γ_ϵ is usually taken[8] to have an exponential dependence on R. It is adopted here to render the model as simple as possible, in particular, as the validity of localization does not depend on the nature of Γ_ϵ.

Computations are made for $d\sigma^{(0)}/d\epsilon$ (zeroth partial wave) for a range of values of ϵ between 0.155 and 0.19 au according to eq 21 and 27. For a particular value of ϵ, the classical trajectory is obtained by propagation on the potential curve $W_1 + \epsilon$, using Hamilton's equations of motion. The choice of the potential surface follows as a consequence of eq 10. The initial kinetic energy E_i for the trajectory corresponding to a given ϵ is then given by

$$E_i = E_t + E_0 - \epsilon \quad (42)$$

where E_t is the actual initial kinetic energy with respect to the potential curve $W_2(R)$. For the present computations this is chosen to be

$$E_t = 0.061 \quad (43)$$

The reduced mass of the He-Ar system used here is given by

$$\mu = 6631.406 \quad (44)$$

Propagation is initiated at the internuclear distance $R = 20.0$ in the approaching phase and carried out until $R \sim 20.0$ in the separating phase. Results are obtained for (i)

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(12) W. H. Miller, *Adv. Chem. Phys.*, 25, 69 (1974).

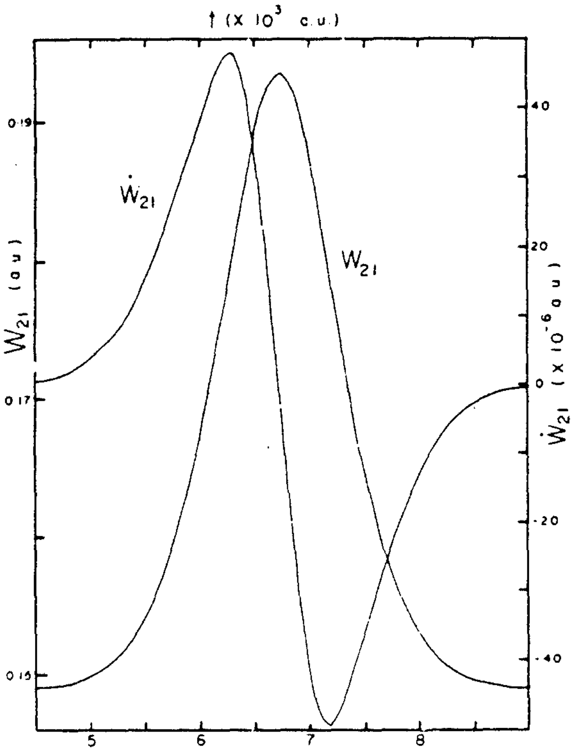

Figure 2. W_{21} and $\dot{W}_{21}$ as functions of time for total initial kinetic energy E_i = 0 [illegible] and ϵ = 0.19. All quantities are in atomic units. Results are obtained by propagating Hamilton's equations with a time step size Δt = 10 au.

the direct numerical trapezoidal quadrature of eq 27, in which case the time step size for the propagation is decreased until the integrated values become convergent, and (ii) the stationary-phase case using eq 28, in which case the time step size is taken to be 10 au. (The total time required for the above-specified trajectory is $\sim 1.3 \times 10^5$.) Figure 2 shows the results for W_{21} and $\dot{W}_{21}$ as a function of time for $\epsilon = 0.19$ au and propagation stepwise $\Delta t = 10$ au.

In Figure 3, the results are presented for $d\sigma^{(0)}/d\epsilon$ (ϵ = 0.155 to 0.19 au) using the two methods of computation—direct numerical quadrature and stationary-phase approximation. These results demonstrate clearly the discrepancy between the two methods, indicating the failure of the stationary-phase approximation, and consequently invalidating the picture of localized interactions. It is, however, interesting to note the qualitative resemblance between the two sets of results.

IV. Discussion

The main conclusion to be drawn from this work is that the Franck–Condon approximation (in the sense stated in the introduction) cannot be applied indiscriminately to bound-continuum problems, such as Penning ionization. This implies that the convenient picture of localized transitions in configuration space does not necessarily hold in molecular collisions involving a continuum of energy eigenstates. We should note, however, that, even though strict localization (at a discrete configuration) has been invalidated "rough" localization may still hold because of the factor $(\epsilon - W_{21} - i\Gamma_\epsilon)^{-1}$ occurring in the integrand of eq 27. But then the degree of localization is much harder to specify than in the stationary-phase case. The strongest statement one can make is that, since $\epsilon - W_{21} - i\Gamma_\epsilon \to 0$ roughly corresponds to the Franck–Condon condition eq 1, the ionizing transition rate peaks at the Franck–Condon points. The extent of the actual "spread" of the transition region remains quite indefinite. Hence, the Franck–Condon approximation, though still useful as a crude estimate of the general vicinity of the transition region, cannot be used as a basic premise justifying strict localization in collision theory. Moreover, in cases where the stationary-phase approximation does apply, strict localization obtains, and, as shown in section II, the Franck–Condon approximation will predict erroneous localization points.

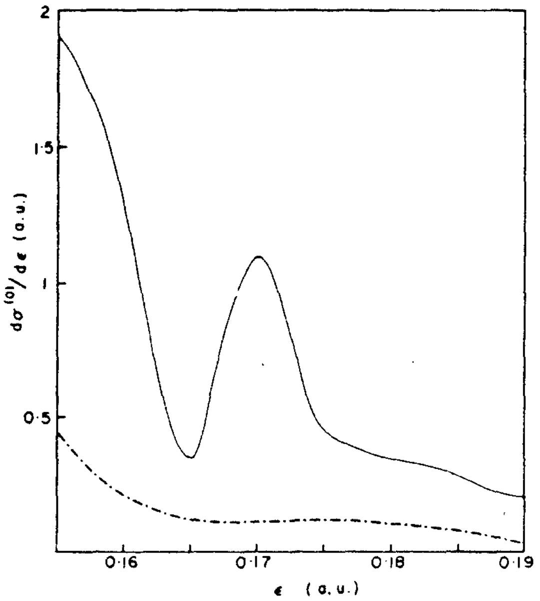

Figure 3. L = 0 partial wave differential ionization cross section $d\sigma^{(0)}/d\epsilon$ as a function of ϵ. The dashed curve is the stationary-phase result, obtained by using eq 25; the solid curve gives the exact result, obtained by numerical quadrature of the integral in eq 24.

Our model for the theory has been chosen to illustrate, under the most simplifying assumptions possible, the inadequacy of the Franck–Condon approximation. As a consequence, some compromise to reality has been made. One such is the assumption of the constancy of Γ_ϵ with respect to R. Since the validity (or lack of it) of the Franck–Condon approximation should not depend on the detailed nature of Γ_ϵ, this assumption has been made in the interest of arriving at the relatively simple form for the differential–integral equation of motion (eq 24) and the subsequent result eq 27. These would require modification if the time (or spatial) variation of Γ_ϵ becomes important. Hence, further work including this effect should prove worthwhile in order to bring the model closer to reality, although the major conclusion is not expected to be changed.

Another worthwhile direction of further investigations would be the nonperturbative treatment of eq 24 via the solution of an integral equation (as mentioned in section II), or the carrying out of the perturbative solution to higher orders. It must be pointed out that we have not attempted here to delineate rigorously the general criteria of validity for the perturbative treatment used. This problem would also appear to warrant further work.

With regard to the physical characteristics of the problem, a natural extension is to include the spin and propagation direction of the emitted electrons as observables. This would entail enlargement of the continuum basis set to include these degrees of freedom, and also some detailed studies of the spin- and direction-dependent configuration-interaction coupling strengths. Finally, it is interesting to point out that, when these extra degrees of freedom are included, the problem becomes formally identical with that of molecular fluorescence in a collision context,[13] in which the photon frequency ω, wave vector direction $\hat{k}$, and polarization direction $\hat{\epsilon}$ correspond to ϵ, $\hat{\mathbf{k}}$ (electronic momentum unit vector), and $\hat{\mathbf{S}}$ (electronic spin unit vector) in the problem of collisional ionization.

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