Probability conservation in theories of collisional ionization and detachment

M. L. Du and J. B. Delos

Physics Department, College of William and Mary, Williamsburg, Virginia 23185

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The semiclassical local-complex-potential theory has been widely used to describe detachment and ionization in atom-atom and ion-atom collisions. However, it has been shown that the resulting formulas do not conserve probability. In this paper, we show that the problem arises from the inconsistent treatment of the effects of interference, tunneling, and diffraction. A more complete theory is based upon the close-coupling expansion, which leads to an infinite set of coupled equations. A method for solving such sets of equations was developed in earlier work. Here we implement that method using a new iterative numerical scheme, and we show that the iteration converges to results in which probability is conserved.

I. INTRODUCTION

The theory of Penning ionization and associative ionization was developed by Nakamura[1] and Miller,[2] and then carried further by Bieniek[3] and Hickman and Morgner.[4] The theory has generally been very successful, both for quantitative calculations of cross sections and for qualitative interpretation of experimental measurements.[5,6] A particularly careful and detailed calculation on the He*-H system was made by Morgner and Niehaus.[7] They showed that the theory was generally in accord with their experimental observations, but at the same time, they noticed a fact that they found rather disturbing: When the total calculated ionization probability was added to the calculated probability of survival of the initial excited state, these quantities did not sum to unity. The discrepancies were not large—their calculated total probabilities varied between 0.96 and 1.05—but these discrepancies demonstrated that the theory is not exact and that it contains errors or inconsistencies which in this case amount to a few percent.

In view of the very high precision of present experiments, it is desirable to develop a more accurate theory that does not contain such inconsistencies. The evidence obtained by Morgner and Niehaus seemed to indicate that the problem lay in the calculated cross sections for associative ionization, so they suggested that the discrepancy might not appear in systems for which associative ionization does not occur.

Electron detachment from negative ions is in some ways quite similar to Penning ionization, and in certain cases essentially the same theory can be used. In calculations on such systems, we have also found total probabilities that do not sum to unity—we will later discuss a case in which the total calculated probability turns out to be 0.65, in error by 35%, quite beyond reasonable expectations of a theory. This case does *not* involve associative detachment, so the problem must be more general than was previously thought. The first purpose of this paper is to identify the source of the problem: we shall show that the problem is inherent in the local-complex-potential ap-

proximation, and that it mainly affects the survival probability. The second purpose is to show that more accurate (in fact, essentially exact) calculations can be made quite easily.

II. SEMICLASSICAL THEORIES

The theory of detachment or ionization can be expressed either in a semiclassical framework or in a fully quantum-mechanical framework. The semiclassical approach is more transparent (and computationally simpler) and it displays very clearly the problem we want to discuss, so we shall use it exclusively. Taking the nuclei to move on a classical trajectory $R(t)$, we assume the following properties of the electronic states.

(1) There is one discrete bound state interacting with a continuum of free states.

(2) Transitions occur from bound to free and from free to bound states, but direct free-to-free transitions are unimportant.

(3) The coupling between bound and free states can be represented "diabatically," as an off-diagonal matrix element of the electronic Hamiltonian. Nonadiabatic coupling matrix elements ($\langle \text{bound} | d/dR | \text{free} \rangle$ as well as $\langle \text{free} | d/dR | \text{free}' \rangle$) are negligible.

Under these assumptions, denoting $b_{-1}(t)$ as the probability amplitude for finding the electron in the bound state, and $b_\epsilon(t)$ as the amplitude for finding it in the free state with energy ϵ, then these coefficients obey the infinite set of close-coupled equations,

$$i\hbar \frac{d}{dt}b_{-1}(t) = h_{-1,-1}(t)b_{-1}(t) + \int_0^\infty h_{-1,\epsilon}(t)b_\epsilon(t)\rho_\epsilon d\epsilon ,$$

$$i\hbar \frac{d}{dt}b_\epsilon(t) = h_{\epsilon,\epsilon}(t)b_\epsilon(t) + h_{\epsilon,-1}(t)b_{-1}(t) ,$$

(1)

where ρ_ϵ is the density of states in the continuum. Here $h_{-1,-1}$ is the energy of the bound state [the quantity called $V^*(R(t))$ in Penning ionization theory], $h_{0,0}$ is the lowest free state $[V^+(R(t))]$, ϵ is the energy of the escaping electron, $h_{\epsilon,\epsilon} = h_{0,0} + \epsilon$, and $h_{-1,\epsilon}$ is the matrix element of the electronic Hamiltonian between the bound state and the free state of energy ϵ (Fig. 1).
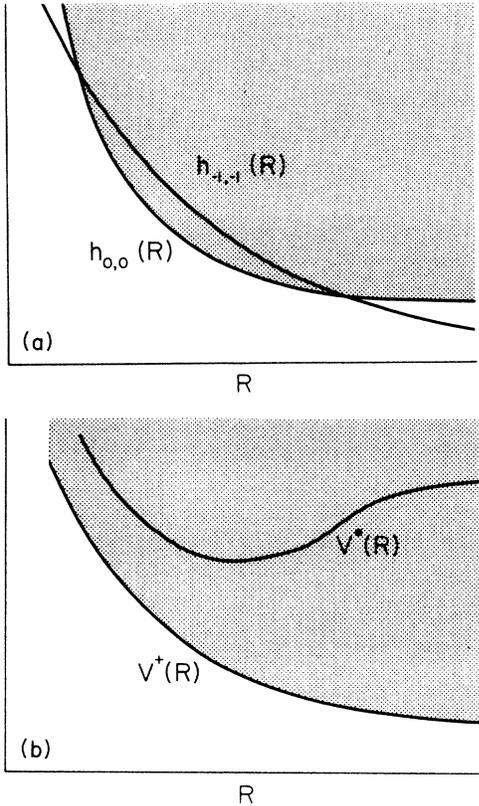
FIG. 1. Typical form of energy curves for (a) electron detachment from negative ion, $h_{-1,-1}(R)$ is the negative ion curve $(AB)^-$ and $h_{0,0}(R)$ is the neutral (AB); (b) Penning ionization, $V^*(R)$ is the excited state of the neutral $(AB)^*$ and $V^+(R)$ represents the ion $(AB)^+$.

The above assumptions have been stated with more precision and discussed at length in Refs. 8(a) and 8(d). These assumptions are widely accepted, and they underlie all of the work considered here.[1-8,9] Our purpose now is to examine the approximations that have been used to solve the resulting close-coupled equations (1).

Equations (1) have a Hermitian "matrix" on the right-hand side $(h_{-1,\epsilon} = h^*_{\epsilon,-1})$, so it follows that they conserve probability

$$|b_{-1}(t)|^2 + \int_0^\infty |b_\epsilon(t)|^2 \rho_\epsilon d\epsilon = 1 \ . \tag{2}$$

A phase change

$$b_{-1}(t) = c_{-1}(t)\exp\left[-i \int_{t_0}^t h_{0,0}(t')dt'/\hbar\right] ,$$

$$b_\epsilon(t) = c_\epsilon(t)\exp\left[-i \int_{t_0}^t h_{0,0}(t')dt'/\hbar\right] \tag{3}$$

preserves this property, but changes the form of the equations to

$$i\hbar\frac{d}{dt}c_{-1}(t) = \Delta(t)c_{-1}(t) + \int_0^\infty h_{-1,\epsilon}(t)c_\epsilon(t)\rho_\epsilon d\epsilon , \tag{4a}$$

$$i\hbar\frac{d}{dt}c_\epsilon(t) = \epsilon c_\epsilon(t) + h_{\epsilon,-1}(t)c_{-1}(t) , \tag{4b}$$

where $\Delta(t) = h_{-1,-1}(t) - h_{0,0}(t)$ is the energy gap between the bound state and the lowest free state.

The first step in solving these equations is to relate $c_\epsilon(t)$ to $c_{-1}(t)$ using (4b):

$$c_\epsilon(t) = (i\hbar)^{-1} \int_{t_0}^t \exp[-i\epsilon(t-t')/\hbar]$$
$$\times h_{\epsilon,-1}(t')c_{-1}(t')dt' , \tag{5}$$

where we have used the initial condition $c_\epsilon(t_0) = 0$. Now if we have any approximation for $c_{-1}(t)$, then evaluation of this integral gives $c_\epsilon(t)$, and the probability that the electron escapes with energy ϵ is

$$P_D(\epsilon) = |c_\epsilon(t = \infty)|^2 \rho_\epsilon . \tag{6}$$

III. CLASSICAL AND SEMICLASSICAL LOCAL-COMPLEX-POTENTIAL APPROXIMATIONS

The local-complex-potential approximation is obtained by taking

$$c_{-1}(t) = \exp\left[-i \int_{t_0}^t \mathscr{E}_{\text{local}}(t')dt'/\hbar\right] , \tag{7}$$

where

$$\mathscr{E}_{\text{local}}(t) = \Delta(t) + \delta(t) - \frac{i}{2}\Gamma(t) , \tag{8a}$$

$$\Gamma(t) = 2\pi |h_{-1,\Delta(t)}(t)|^2 \rho_{\Delta(t)} , \tag{8b}$$

$$\delta(t) = \mathscr{P}\left[\int_0^\infty \frac{|h_{-1,\epsilon}(t)|^2}{\Delta(t) - \epsilon}\rho_\epsilon d\epsilon\right] . \tag{8c}$$

We refer to $\delta(t) - i\Gamma(t)/2$ as the local complex potential. Its real part $\delta(t)$ corresponds to the "shift" of a resonance state in a continuum, and its imaginary part $\Gamma(t)$ corresponds to the width.[10] In Ref. 8(e), we showed how this formula follows from the close-coupled equations (1) using certain additional approximations.

Let us now put approximation (7) for $c_{-1}(t)$ into Eq. (5) for $c_\epsilon(t)$,

$$c_\epsilon(t) = (i\hbar)^{-1} \int_{t_0}^t h_{\epsilon,-1}(t')\exp\left[\frac{i}{\hbar}\left[\epsilon(t'-t) - \int_{t_0}^{t'} \mathscr{E}_{\text{local}}(t'')dt''\right]\right]dt' \tag{9}$$

and evaluate the integral using the stationary-phase method, assuming $\delta(t)$ and $\Gamma(t)$ are much smaller than $\Delta(t)$. The stationary-phase points $\hat{t}_n(\epsilon)$ occur when

$$\Delta(\hat{t}_n(\epsilon)) = \epsilon \tag{10}$$

and the contribution of each stationary-phase region to the integral is

$$(i\hbar)^{-1}h_{-1,\epsilon}(\hat{t}_n(\epsilon))\left[\frac{2\pi\hbar}{\left|\dfrac{d\Delta(\hat{t}_n(\epsilon))}{dt}\right|}\right]^{1/2}\exp\left[\frac{i}{\hbar}\left[\epsilon[\hat{t}_n(\epsilon)-t]-\int_{t_0}^{\hat{t}_n(\epsilon)}\mathscr{S}(t'')dt''\right]-i\frac{\pi}{4}\mathrm{sgn}\left[\frac{d\Delta(\hat{t}_n(\epsilon))}{dt}\right]\right].\qquad(11)$$

Summing over the stationary-phase points and neglecting interference between them, we obtain

$$|c_\epsilon(\infty)|^2\rho_\epsilon=\sum_n\left[\hbar\Gamma(\hat{t}_n(\epsilon))\Big/\left|\frac{d\Delta}{dt}\right|_{\hat{t}_n(\epsilon)}\right]$$

$$\times\exp\left[-\int_{t_0}^{\hat{t}_n(\epsilon)}\Gamma(t'')dt''/\hbar\right],\qquad(12)$$

and of course

$$|c_{-1}(\infty)|^2=\exp\left[-\int_{t_0}^{\infty}\Gamma(t'')dt''/\hbar\right].\qquad(13)$$

We refer to Eqs. (12) and (13) as the classical local-complex-potential formulas. It is not difficult to verify that these equations exactly conserve probability. However, they have other well-known defects: they do not describe interference between transitions taking place on incoming and outgoing parts of the trajectory, they do not describe "classically forbidden" transitions to free states with ϵ outside the range of values of $\Delta(t)$, and they give singular behavior in the electron-energy spectrum at those values of ϵ such that $(d\Delta/dt)|_{\hat{t}_n(\epsilon)}=0$.

These defects are easily remedied, as Miller showed long ago.[2] For the "allowed" values of ϵ well away from any extremum of $\Delta(t)$, one can use the full stationary-phase result (11), and include interference effects when summing over stationary-phase points $\hat{t}_n(\epsilon)$. For "forbidden" values of ϵ, distortion of the contour of t-integration so that it passes through complex stationary-phase points gives an exponentially decreasing probability of excitation of such states. Finally a uniform Airy-function formula properly describes the diffractive smoothing of the "rainbow" at the boundary between allowed and forbidden regions of ϵ. Alternatively, we may continue to use the local approximation (7) and (8), but evaluate integral (5) exactly by numerical quadrature. This last approach is what we shall call the "semiclassical" local-complex-potential method.

These methods correct the defects of the classical local-complex-potential formula, but they create a problem—probability is not conserved. The reason is obvious: the quantum effects of interference, tunneling, and diffraction are incorporated into the formula for $c_\epsilon(t)$; in principle those phenomena must also have some consequences for $c_{-1}(t)$, but these consequences are being neglected. This inconsistent treatment of c_ϵ and c_{-1} causes a violation of unitarity. Numerical results shown in a later section will display this quite clearly.

IV. EXACT SOLUTION TO THE CLOSE-COUPLED EQUATIONS

It turns out to be surprisingly easy to obtain an essentially exact solution to the close-coupled equations (4). Using (5) in (4a) and inverting the order of integration over t' and ϵ, we obtain a single integro-differential equation for c_{-1}:

$$i\hbar\frac{d}{dt}c_{-1}(t)=\Delta(t)c_{-1}(t)+\int_{t_0}^{t}\mathscr{G}(t,t')c_{-1}(t')dt',\qquad(14)$$

where

$$\mathscr{G}(t,t')=(i\hbar)^{-1}\int_0^{\infty}h_{-1,\epsilon}(t)h_{\epsilon,-1}(t')$$
$$\times e^{-i\epsilon(t-t')/\hbar}\rho_\epsilon d\epsilon.\qquad(15)$$

If we now *define* $\mathscr{S}(t)$ by the formula

$$c_{-1}(t)=\exp\left[-i\int_{t_0}^{t}\mathscr{S}(t')dt'/\hbar\right],\qquad(16)$$

we find from (14) that $\mathscr{S}(t)$ obeys the integral equation

$$\mathscr{S}(t)=\Delta(t)+\int_{t_0}^{t}\mathscr{G}(t,t')\exp\left[i\int_{t'}^{t}\mathscr{S}(t'')dt''/\hbar\right]dt'.\qquad(17)$$

This equation can be solved by iteration:

$$\mathscr{S}^{(0)}(t)=\Delta(t),$$

$$\mathscr{S}^{(1)}(t)=\Delta(t)+\int_{t_0}^{t}\mathscr{G}(t,t')\exp\left[i\int_{t'}^{t}\Delta(t'')dt''/\hbar\right]dt',\qquad(18)$$

$$\mathscr{S}^{(n+1)}(t)=\Delta(t)+\int_{t_0}^{t}\mathscr{G}(t,t')\exp\left[i\int_{t'}^{t}\mathscr{S}^{(n)}(t'')dt''/\hbar\right]dt'.$$

This iterative procedure was proposed in Ref. 8(e) and implemented there and in Ref. 8(f), but only through first order. In the present paper we carry the iterative procedure to sufficiently high order to obtain convergence.

A converged $\mathscr{S}(t)$ must represent an exact solution to Eq. (17); using (16) it must give an exact solution to the integro-differential equation (14), and this together with (15) must give an exact solution to the close-coupled equations (4). Hence the probabilities calculated by this method must sum to unity. For slow collisions, as was shown in Ref. 8(d), the exact $\mathscr{S}(t)$ approaches $\mathscr{S}_{local}(t)$, but where $\mathscr{S}_{local}$ has discontinuous derivatives, $\mathscr{S}(t)$ has smooth oscillations. In this way $\mathscr{S}(t)$ incorporates the effects that interference, tunneling, and diffraction have upon $c_{-1}(t)$.

V. MODEL AND CALCULATIONAL METHODS

We shall present in detail a case we encountered while examining the H^--He collision system. In this case, the local approximation and also the first-order approximation give unsatisfactory results, and higher-order calculations are needed.

The "input" to the calculation is the pair of functions $\Delta(t)$ and $\mathscr{G}(t,t')$. The energy gap $\Delta(R)$ was obtained using the calculation by Olson and Liu.[11,12] Specifically $\Delta(R)=h_{-1,-1}(R)-h_{0,0}(R)$, and each of these functions was taken as follows: (i) For $R>6.0$, $h_{-1,-1}=0.0$, $h_{0,0}=0.75$ eV; (ii) for $0.75\le R \le 6.0$, a spline fit to the Hartree-Fock calculation by Olson and Liu was used; (iii) for $R<0.75$, $h_{0,0}$ and $h_{-1,-1}$ were taken to be a_i+b_i/R^2 with a_i and b_i chosen so that this form matches the value and the derivative of the spline functions at $R=0.75$; the resulting $\Delta(R)$ is shown in Fig. 2.

The trajectory function $R(t)$ was calculated using an average potential energy,

$$\overline{V}(R)=\tfrac{1}{2}[h_{-1,-1}(R)+h_{0,0}(R)]$$
$$-\tfrac{1}{2}[h_{-1,-1}(\infty)+h_{0,0}(\infty)] \tag{19}$$

with

$$\frac{dR}{dt}=\left\{\frac{2}{\mu}[E-\overline{V}(R)-Eb^2/R^2]\right\}^{1/2} .$$

Results will be presented for the trajectory having $E=4.0$ eV (c.m.) and $b=1.6$ bohrs.

The propagator $\mathscr{G}(t,t')$ is related to the coupling between bound and free states by Eq. (15). For these coupling matrix elements we used a separable approximation (i.e., we assumed that they all have the same R dependence),

$$h_{-1,\epsilon}(R)=g(R)V_{-1,\epsilon} . \tag{20a}$$

For the R dependence we chose the form

$$g(R)=A\exp(-BR) \tag{20b}$$

with parameters $A=2.5$, $B=0.3$ (atomic units here and below, except where indicated otherwise). Now from Eq. (15) one finds that $V_{-1,\epsilon}$ enters the theory only in the combination $|V_{-1,\epsilon}|^2 \rho_\epsilon$, and for the ϵ dependence of this quantity we took

$$|V_{-1,\epsilon}|^2\rho_\epsilon=C\epsilon^{1/2}e^{-D\epsilon} \tag{21}$$

with $C=0.01$, $D=12.0$. As shown in Fig. 3, this quantity is similar to corresponding quantities we had obtained in earlier papers using square-well models, but the clean analytic form (21) greatly simplifies the calculations. Using (21) in (15), we obtain

$$\mathscr{G}(t,t')=g(R(t))g(R(t'))\hat{\mathscr{G}}(t-t') , \tag{22a}$$

where

$$\hat{\mathscr{G}}(\tau)=(C/i\hbar)\int_0^\infty \epsilon^{1/2}\exp[-(D+i\tau/\hbar)\epsilon]d\epsilon \tag{22b}$$

$$=(-iC\pi^{1/2}/2\hbar)\exp[-\tfrac{3}{2}i\tan^{-1}(\tau/D\hbar)]$$

$$\times(D^2+\tau^2/\hbar^2)^{-3/4} \tag{22c}$$

(the substitution $\epsilon=x^2$ reduces the integral to a standard form). Computations are further simplified by introduction of a "reduced time" variable z, defined as

$$z=v_0t , \tag{23a}$$

$$v_0=(2E/\mu)^{1/2} . \tag{23b}$$

All of the basic equations can be rewritten using z instead of t as the independent variable, and when this is done, one finds that the energy dependence of most quantities is made less strong. For example, the significant range of the time integration depends upon the energy, but since z is closely related to internuclear distance, the significant range of integration over z is essentially independent of energy.

Now given $\Delta(R)$, $g(R)$, and $\hat{\mathscr{G}}(t-t')$, for each value of energy E and impact parameter b, the following computational procedure is used.

(1) $R(z)$ is calculated by integration of the equation

$$\frac{dR}{dz}=[1-\overline{V}(R)/E-b^2/R^2]^{1/2} . \tag{24}$$

FIG. 2. The energy gap $\Delta(R)$. A spline fitting reproduces the result of Olson and Liu for $0.75<R<6.0$, and straightforward extrapolations extend it to smaller and larger r regions. R_{tp} is the turning point.
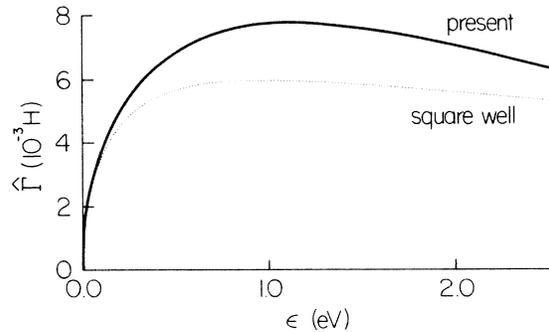
FIG. 3. $\hat{\Gamma}=2\pi|V_{\epsilon,-1}|^2\rho_\epsilon$. Solid line: Analytic form (21). Dotted line: square-well model defined in Ref. 8(d), multiplied by a constant such that the two forms agree in the limit of small ϵ. The two are similar in their ϵ dependence, but the analytic form greatly simplifies the computations. (In the present calculations, we also took the magnitude of $\hat{\Gamma}$ to be smaller than that in earlier calculations.)

For $0 < z < 8.0$, the result is fit by a spline. For $z > 8.0$, we take

$$R(z) = [b^2 + (z + z_d)^2]^{1/2} \tag{25}$$

with z_d calculated by matching (25) to the spline fit. Since $R(z)$ is a symmetric function, it is now available for all z.

(2) A function $\Phi^0(z)$ is calculated by integration

$$\Phi^0(z) = \int_0^z \Delta(z') dz' . \tag{26}$$

This is also fit to a spline for $z < 8.0$, and for $z > 8.0$ it is taken to be

$$\Phi^0(z) = \Phi^0(8.0) + (z - 8.0)\Delta(\infty) . \tag{27}$$

Since $\Phi^0(z)$ is an antisymmetric function, it is available for all z.

(3) $\mathscr{E}^{(1)}(z)$ is computed by integration of the equation

$$\mathscr{E}^{(1)}(z) = \Delta(R(z)) + g(R(z)) \int_0^{z - z_0} \mathscr{G}(\hat{z}/v_0) g(R(z - \hat{z})) \exp\{(i/v_0)[\Phi^0(z) - \Phi^0(z - \hat{z})]\} d\hat{z}/v_0 . \tag{28}$$

A file is built containing 401 values of $\mathscr{E}^{(1)}$ for evenly spaced values of z from $z = -12.0$ to 18.0. The step size for the integration is chosen such that there would be at least 10 points in each oscillation of the exponential in Eq. (28), and ten points in the region where $\mathscr{G}(z)$ is rapidly changing.

(4) Now the function $\Phi^1(z)$ is computed by integration of the equation

$$\Phi^1(z) = \int_{-12.0}^z \mathscr{E}^{(1)}(z') dz' . \tag{29}$$

This is tabulated at the same set of 401 points, and then a spline fit is used for interpolation.

(5) The function $\mathscr{E}^{(2)}$ is computed by integration of Eq. (28), with Φ^1 replacing Φ^0. This procedure is iterated until satisfactory convergence is obtained. In the present case (which is one of the worst we have come across) the fourth iteration gives excellent results.

(6) From the final $\mathscr{E}(z)$, $c_{-1}(z)$ is calculated by integration of a differential equation derived from Eq. (16):

$$\frac{dc_{-1}(z)}{dz} = -i\mathscr{E}(z)c_{-1}(z)/v_0 . \tag{30}$$

We take $P_s = |c_{-1}(z = 18.0)|^2$. To obtain the electron energy spectrum, we define

$$c'_\epsilon(z) = c_\epsilon(z)\rho_\epsilon^{1/2}\exp(i\epsilon z/v_0) . \tag{31}$$

This quantity is calculated by integration of

$$\frac{dc'_\epsilon(z)}{dz} = -i(|V_{-1,\epsilon}|^2\rho_\epsilon)^{1/2} g(R(z))e^{i\epsilon z/v_0} c_{-1}(z)/v_0 \tag{32}$$

which is derived from Eq. (4b). Then $P_D = |c'_\epsilon(z = 18.0)|^2$. A fourth-order Runge-Kutta method is used for these integrations.

VI. RESULTS

Figures 4(a) and 4(b) show, respectively, the real and imaginary parts of $\mathscr{E}(t)$, comparing the local, first-order, and converged (fourth-order) results. Convergence is established partly by the fact that the third- and fourth-order functions differ by less than the thickness of the line in the figures. As was found in earlier work, the local re-

sult has discontinuous derivatives at the points where the discrete state crosses into the continuum, but the first-order and exact results show smooth oscillations in these regions.

In Table I we present the total detachment probability and the survival probability as calculated by the local ap-
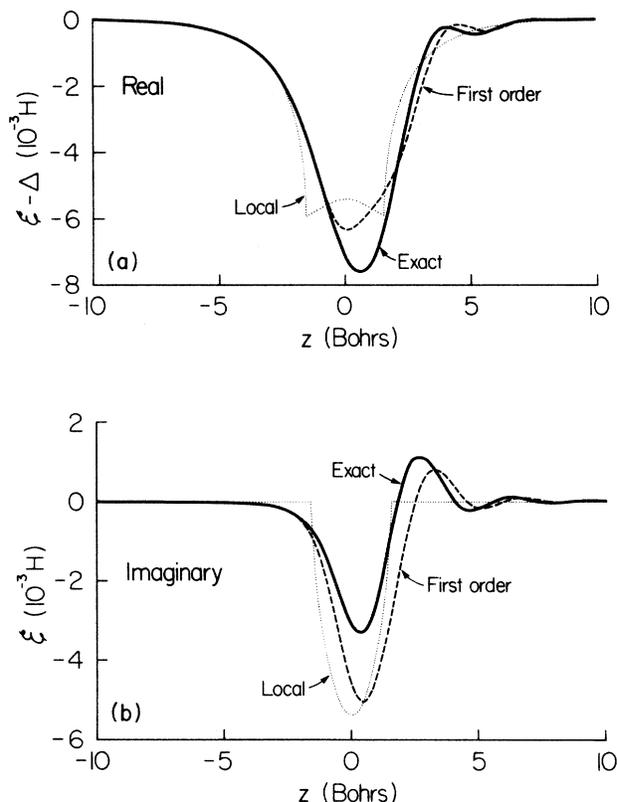
FIG. 4. $\mathscr{E}(z) - \Delta(z)$: fourth order (——); first order (— — —); local approximation ($\cdots$). The "local approximation" has sharp corners at the points where the bound-state curve crosses into the continuum. The "first order" and "fourth order" are smoother than the local approximation and they oscillate about it. The fourth order can be regarded as the "exact" solution of Eq. (17).

TABLE I. Survival and detachment probabilities and their sum. The total probability in the last column shows clearly the convergence of the iteration method. Note also that in all cases the detachment probability is more accurate than the survival probability.

	P_D	P_S	$P_D + P_S$
Local approximation	0.4849	0.1720	0.6569
First order	0.5461	0.1819	0.7280
Second order	0.5703	0.3965	0.9668
Third order	0.5870	0.4344	1.0214
Fourth order	0.5890	0.4128	1.0018
Corrected first order	0.5461	0.4539	1.0000

proximation and in each order of the iterative procedure. One sees that for the local approximation these quantities sum to 0.66 instead of 1.0. Convergence of this sum to unity in the iterative calculation is clearly displayed. Most interesting is the fact that the greatest error is in the survival probability—the local result is almost $2\frac{1}{2}$ times too small, and the first-order result is scarcely better. The detachment probability is more respectable—the local result is in error by 0.1 and the first-order result by 0.04 out of 0.59. This suggests that reasonable results can be obtained using less computer time by accepting the first-order calculation for the detachment probability, and setting the survival probability to $1-P_D$. This "corrected first-order" result is also shown in the Table I.

The (doubly differential) electron-energy spectrum is shown in Fig. 5. One finds that the local and first-order approximations reproduce quite well the shape of the energy spectrum, but they give a magnitude that is somewhat small, as already found in Table I.

VII. SUMMARY AND CONCLUSION

The failure of probability conservation is a general feature of semiclassical local-complex-potential theories of detachment and ionization. The problem arises because the quantum effects such as interference, tunneling, and diffraction are included in the calculation of the detached-electron-energy spectrum, but they are ignored in the calculation of the survival probability. Because of this inconsistency, the total detachment and survival probabilities do not sum to unity.
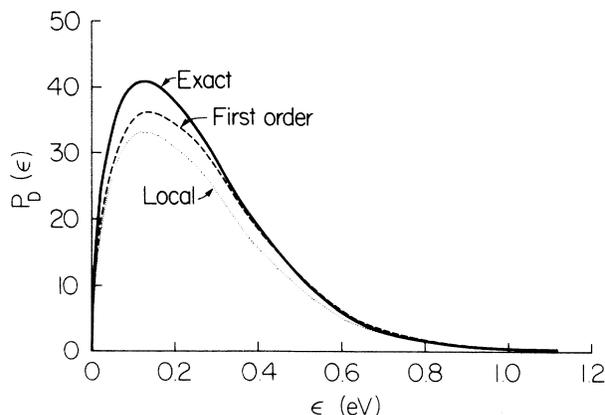
FIG. 5. The detached-electron-energy spectrum calculated by fourth order (———), first order (— — —), and local approximation ($\cdots$). These are "doubly differential" spectra, associated with a specific trajectory having $E=4$ eV, $b=1.6$ bohrs. The curves have similar shapes, but the local approximation is about 20% smaller than the exact (fourth-order) result. The first-order result generally lies between them.

Ionization and detachment can be described more completely by an infinite set of close-coupled equations. We have developed an iterative method that gives an essentially exact solution to this set of equations, and results of this method have been presented for a case that arises in the H^--He system.

In most of the cases we have studied, we have found that the detachment probability calculated from the local approximation is reasonably accurate, and the error is almost entirely in the survival probability. Therefore the simplest way to correct the problem is to compute P_D by the local approximation and set $P_S = 1-P_D$. On the other hand, if accuracy is important, then the iterative calculation of $\mathscr{E}(t)$ is necessary. Another method, intermediate in difficulty and accuracy, is to calculate $\mathscr{E}(t)$ to first order, and then adjust the survival probability if necessary. We have used this last approach in calculations on the H^--He system that will be reported in a future publication.

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[9]Neither Miller (Ref. 2) nor Nakamura (Ref. 1) stated these assumptions explicitly. Nakamura mentions Fano's theory of configuration interaction with a continuum, while Miller only cites Messiah's derivation of the "golden rule." These approaches only make sense if the stated assumptions are accepted.

[10]$\hat{\Gamma}(t)$ depends upon time in two ways: through the explicit dependence of $h_{-1,\epsilon}(R)$ on the internuclear position $R(t)$, and through the dependence on ϵ, which is set equal to $\Delta(t)$ in Eq. (8b).

[11]R. E. Olson and B. Liu, Phys. Rev. A 17, 1568 (1978).

[12]Olson and Liu made a Hartree-Fock (HF) calculation for $R > 0.75$, and a more accurate configuration-interaction calculation for $R > 1.5$. Because we needed the energy gap over the larger range, we chose to use their HF data.

FIG. 1. Typical form of energy curves for (a) electron detachment from negative ion, $h_{-1,-1}(R)$ is the negative ion curve $(AB)^-$ and $h_{0,0}(R)$ is the neutral (AB); (b) Penning ionization, $V^*(R)$ is the excited state of the neutral $(AB)^*$ and $V^+(R)$ represents the ion $(AB)^+$.