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TECHNICAL REPORT NO. 2

SQUARE WAVE VOLTAMMETRY

AT THE DROPPING MERCURY

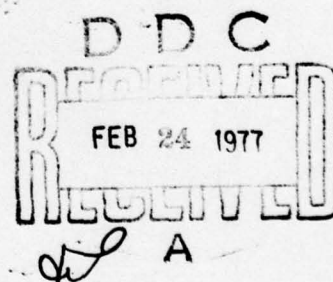
ELECTRODE: THEORETICAL

by

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BRIEF

The theoretical response for the application of square wave voltammetry at a dropping mercury electrode is presented, with particular reference to points of current measurement.

ABSTRACT

The theoretical aspects of square wave voltammetry at the dropping mercury electrode are presented. The technique involves scanning the entire potential range of interest on a single drop of a dme. Asymmetries in the waveform as well as variations in current measurement parameters are discussed. Indications are that previous uses of the waveform may not have utilized all its capabilities.

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For the past several years, we have been concerned with development and application of pulse polarography and voltammetry (1). The advantages of these pulse techniques reside chiefly in their discrimination against double layer charging currents, but, as they are usually applied, they are relatively slow: only one measurement is made per drop of the dme and a ratio of delay time to pulse time of 10:1 or greater is normally employed.

Recently a modification to the PAR 174 was introduced (2) which allows it to do a fast sweep mode of differential pulse polarography. One of the problems inherent with this modification arises from the linear ramp used as the base potential sweeping function. The required high slope of the linear ramp reintroduces charging current background that the differential pulse technique was intended to discriminate against. This fast sweep technique also suffers from resolution problems at sweep rates greater than 200 mV/sec in that insufficient points are taken to define the peaks.

We now turn to the technique of square wave voltammetry at the dme which retains a high discrimination against double layer charging current but which allows measurement of a complete potential range during the life of a single drop at the dme. This technique was reported by Barker (3) as long ago as 1957, but has since seen little application. Ramaley and Krause have developed the theory (4) and have presented some application (5) of square wave voltammetry at the hanging mercury drop electrode.

The discussions of Ramaley and Krause were limited to small step heights (and consequent slow scan rates). In order to carry out experiments within the life of a single drop of a DME, faster scan rates (>100 mV/sec) are required. Faster scan rates imply relatively larger step heights for the underlying staircase wave-form. While the equations presented below are valid for all values of experimental parameters, our calculations concentrate on those values which are useful in our particular case.

Our fundamental potential wave-form differs superficially from that of Ramaley and Krause in that the phase of the square wave is shifted by π relative to the staircase. Our treatment also includes the possibility of some asymmetries in wave-form and measurement times not considered by Ramaley and Krause.

We develop our treatment for a stationary planar electrode; it is shown in a later paper (6) that the effects of drop growth can be well compensated by an area normalization of the observed currents.

The general square wave-form, shown in Figure 1, can be thought of as a pair of pulses superimposed on a staircase wave-form. One of the pulses is coincident with the step advance of the staircase, while the other is in the opposite sense and lasts until the end of the potential step. In the work of Ramaley (4,5), the first pulse is opposite in sense to the staircase direction while in our case the pulse coincident with staircase advance is in the ascending staircase scan direction. In the work presented here, the two pulses are of equal amplitude (with respect to the basic staircase) but need not be of equal duration.

The nomenclature we use is adapted from that of staircase voltammetry (7) and differs somewhat from that of Barker (8) and Ramaley (4,5). The basic time unit, τ , corresponds to the step width in staircase voltammetry and ΔE is the step height. For the square wave-form, some additional parameters must be introduced as shown in Figure 1. The square wave amplitude is E_{sw} and corresponds to the magnitude of each of the two potential pulses (with respect to the staircase potential). The fraction of each period during which the potential is "up" is σ ; the length of the forward pulse therefore is $\sigma\tau$. The current is measured twice during each staircase period: at time $\rho_1\tau$ during the forward pulse and at time $\rho_2\tau$ during the reverse pulse. The coefficient ρ_1 , ρ_2 , and σ are all fractions less than unity and

$\rho_1 < \sigma < \rho_2$. The treatment of Ramaley and Krause was restricted to the symmetric case in which $\sigma = 0.5$ and $\rho_1 = \rho_2 - \sigma$. The usual output is the difference in current measurement at $\rho_1 \tau$ and $\rho_2 \tau$ during the same staircase period, which we call the forward difference and designate ΔI^+ , but other differencing schemes are possible.

Assuming semi-infinite linear diffusion and a reversible electrode reaction with only the oxidized form initially present in solution, the equation for the currents can be obtained by straight-forward application of the superposition theorem (9) or by generalization and modification of the arbitrary wave-form equation presented by Rifkin and Evans (10).

During the j th period of the staircase, the current measured at $\rho_1 \tau$ during the forward pulse is

$$I_f(j) = \frac{nFAD_0^{1/2}}{\sqrt{\pi\tau}} \left\{ \frac{C_2(j-1) - C_1(j)}{\rho_1^{1/2}} + \sum_{m=0}^{j-1} \frac{C_2(m-1) - C_1(m)}{(j-m+\rho_1)^{1/2}} + \frac{C_1(m) - C_2(m)}{(j-m+\rho_1-\sigma)^{1/2}} \right\} \quad (1)$$

and the current at $\rho_2 \tau$ during the reverse pulse is

$$I_r(j) = \frac{nFAD_0^{1/2}}{\sqrt{\pi\tau}} \sum_{m=0}^j \left\{ \frac{C_2(m-1) - C_1(m)}{(j-m+\rho_2)^{1/2}} + \frac{C_1(m) - C_2(m)}{(j-m+\rho_2-\sigma)^{1/2}} \right\} \quad (2)$$

In Equations (1) and (2), the terms of the type $C_1(k)$ are the surface concentration of oxidant during the forward pulse of the k th period. Terms of the form $C_2(k-1)$ and $C_2(k)$ are the surface concentrations during the reverse pulses of the $(k-1)$ and k th periods, respectively. Numbering of the periods starts with $j=0$ and $C_2(-1)$ (for the first period) is the bulk concentration C^* .

For a planar electrode and a simple reversible reaction, the surface concentration of oxidant is fixed by the potential

$$C_o(0,t) = \frac{C^*}{1+\epsilon(t)} \quad (3)$$

where

$$\epsilon(t) = \exp \left\{ -\frac{nF}{RT} [E(t) - E_{1/2}^r] \right\} \quad (4)$$

and $E_{1/2}^r$ is the reversible half wave potential.

Combining the potential wave-forms:

$$E_1(k) = E_i - k\Delta E - E_{sw} \quad (5)$$

during the forward pulse and

$$E_2(k) = E_i - k\Delta E + E_{sw} \quad (6)$$

during the reverse pulse with Equation (3) giving the explicit surface concentration to be used in Equations (1) and (2).

The forward current can then be written

$$I_f(j) = \frac{nFAD_0^{1/2}C^*}{\sqrt{\pi\tau}} \psi_f(E_{sw}, \Delta E, \rho_1, \sigma) \quad (7)$$

and the reverse current

$$I_r(j) = \frac{nFAD_0^{1/2}C^*}{\sqrt{\pi\tau}} \psi_r(E_{sw}, \Delta E, \rho_2, \sigma) \quad (8)$$

The forward difference current is

$$\Delta I^+(j) = I_f(j) - I_r(j) = \frac{nFAD_0^{1/2}C^*}{\sqrt{\pi\tau}} (\psi_f(j) - \psi_r(j)) = \frac{nFAD_0^{1/2}C^*}{\sqrt{\pi\tau}} \Delta\psi^+(j) \quad (9)$$

The explicit formulation of the ψ functions can be written by combining Equations (5) and (6) with Equations (3) and (4) and substituting the results into Equations (1) and (2).

Theoretical square wave voltammograms were generated for a variety of experimental parameters. The computer program explicitly calculates and stores the component forward and reverse current functions ψ_f and ψ_r rather than merely the difference function $\Delta\psi^+$. Consideration of the partial currents greatly facilitates the understanding of the results. The program was written in Fortran IV and was run on Digital Equipment Corp. PDP-12 computer.

Calculated square wave current-potential functions for several values of E_{sw} are shown in Figure 2. The difference current is always an essentially symmetric peak shaped function, but for small square wave amplitude is smaller than either the forward or reverse currents (Figure 2A). The effect of square wave amplitude on the component currents and on the difference current is clearly shown in Figure 3. Only for $n E_{sw} > \sim 15$ mV does the reverse current in the vicinity of the half-wave potential become negative and the difference current become larger in magnitude than the forward current.

The obvious conclusion is that analytical response can be increased by using larger square wave amplitude, but, as in pulse voltammetry, increased amplitudes lead to broadening of the observed current peak. This effect is shown in Figure 4. The analytical choice must therefore be the largest value of square wave amplitude and step height consistent with adequate peak definition and evaluation. Of note in Figure 4 is the increase in the width of the current peak as the square wave amplitude becomes smaller than the step height.

The step height has little effect on the height of the current peak. For a square wave amplitude of 20 mV the peak current function $\Delta\psi_{max}^+$ goes from 0.642 for an $n\Delta E = 1$ mV to 0.686 for an $n\Delta E = 10$ mV ($\sigma = 5$, $\rho_1 = .499$, $\rho_2 = .999$). The individual forward and reverse currents, on the other hand, are markedly affected by the increase in step height. This is shown in Figure 5. The forward current function increases when the step height is increased but the reverse current function also increases, becoming less negative. The magnitude of change for both currents is approximately the same, so the difference current remains relatively unchanged.

Figure 5 is for constant τ , therefore the sweep rate is increasing as the step height is increased. It is interesting to note that increasing the sweep rate by increasing the step height has little effect on the difference

current function. Increasing the sweep rate by decreasing τ will cause the current to increase as $1/\sqrt{\tau}$ for a reversible system. If we compare two step heights at constant sweep rate, we find a marked difference in $\Delta\psi_{\max}^+$. For example, given a sweep rate of 500 mV/sec that we can generate with a 10 mV step of 20 msec period or a 5 mV step of 10 msec period, the normalized peak current values $\Delta\psi_{\max}^+ (\tau)^{-1/2}$ for these are 4.85 and 6.64 respectively.

The important thing to remember is that the peak current will not only depend on the sweep rate but also on how that sweep rate is generated. Decreasing τ to obtain a faster sweep rate is better than increasing ΔE . The values of τ that can be used will, of course, depend on the system response.

The effect of measurement time is shown in Figure 6. These curves are calculated for a symmetric square wave ($\sigma=0.5$) and symmetric measurement times: $\rho_2 = \sigma + \rho_1$. As the measurement time is moved toward the beginning of the pulse, the difference current function greatly increases. As Ramaley and Krause have shown, the increase in peak current obtained by shortening the measurement time is greater than the increase obtained by keeping the measurement times at the end of the pulse and decreasing the staircase period. For the conditions of Figure 6, the peak value of the current function goes as $\rho_1^{-0.6}$ while the peak current depends on $\tau^{-0.5}$.

Some of the effects of asymmetric measurement on an asymmetric square wave are shown in Figure 7. The data for the bottom curve are calculated for variable σ with $\rho_1 = \sigma - 0.001$ and ρ_2 fixed at 0.999. For these conditions, the peak current function is a minimum near $\sigma=0.5$ and increases essentially symmetrically on both sides of the minimum. The plot of the maximum values of $\Delta\psi^+$ vs σ becomes exactly symmetrical as the ratio $\Delta E/E_{sw}$ decreases.

Figure 8 details the individual forward and reverse current functions for three members of the set. For $\sigma = .1$ (Figure 8A) ψ_f is larger than $\Delta\psi^+$ because the reverse current function, ψ_r , has the same sign as ψ_f . This is

due to insufficient material being generated by the forward pulse to allow the reverse reaction to occur during the entire reverse pulse. As σ approaches 1, ψ_r gets more negative with a corresponding reduction in ψ_f until at $\sigma = 0.9$, the reverse pulse is not of sufficient length to regenerate the material consumed during the forward pulse. At this point ψ_f is at its lowest value while ψ_r is at a maximum (negatively). However, the change on ψ_r is greater than the decrease in ψ_f and thus the increase in $\Delta\psi^+$.

The data for the top curve of Figure 7 is again calculated for variable σ , this time with ρ_1 fixed at 0.049 and $\rho_2 = \sigma + 0.049$. ρ_1 and ρ_2 are now positioned close to the switching points where ψ_f and ψ_r are maximum during their individual steps. The peak function $\Delta\psi^+$ is now a maximum at $\sigma = .5$, decreasing almost symmetrically on each side. Again the plot becomes exactly symmetrical at large square wave amplitude to step height ratios.

Individual forward and reverse currents for three members of this set are shown in Figure 9. The trends for the individual current function ψ_f and ψ_r are the same here as in Figure 8. ψ_f decreases and ψ_r increases (negatively) as σ approaches 0.9. However, in contrast to Figure 8 where the negative magnitude of ψ_r changes dramatically as σ goes from 0.1 to 0.9, the change in ψ_r here is relatively small.

Figure 10 illustrates the information that can be gained by a study of the individual forward and reverse current functions. This is a vertical comparison of two members in Figure 7. Here σ and ρ_1 are the same for both figures, equal to .1 and .099 respectively and ρ_2 is varied from close to the switching point (0.149) Fig. 10A to near the end of the step (0.999) Fig. 10B. From examination of the reverse current function, it is obvious that the current during the reverse step has actually changed direction. Directly after the forward step ψ_r is opposite in sign to ψ_f while near the end of the step ψ_f and ψ_r has the same sign. This indicates that the material

generated by the forward pulse has been consumed during the first part of the reverse pulse and in order for the Nernst equation and Fick's laws of diffusion to be obeyed, the current near the end of the step must now flow in the same direction as ψ_f .

There is no obvious reason to output the difference current in which the current at ρ_1 during the j th cycle is differenced with the current at ρ_2 during the same staircase period. Since we have calculated and stored the partial current components, it is a simple matter to examine other differencing schemes, such as the backward difference, $\Delta\psi^-(j) = \psi_f(j) - \psi_r(j-1)$. This difference function has somewhat larger maximum values, especially at smaller square wave amplitudes, as can be inferred from an inspection of the potential dependence of the partial components shown in Figure 2. The apparent peak potential is shifted by approximately one-half the step height, relative to the maximum of the forward difference. Some representative and comparative values of the maximum peak current function ($\Delta\psi_{\max}$), peak potentials and peak widths for forward and backward differences are shown in Table I.

The similarity of this technique to pulse polarography is obvious, although as has been demonstrated, variations in points of measurement affect the shape of the wave. Nevertheless, the equations developed result in wave shapes identical to those for differential pulse polarography (1) at slow scan rates and measurements parameters identical to those employed in pulse polarography.

Work is in progress to develop the theory to include the case of slow electron transfer processes, and first-order chemical processes, including preceeding, following and catalytic reactions.

Experimental verification of the theory presented here and demonstration of the analytical utility of the method at the dropping mercury electrode will be forthcoming (6).

CREDIT

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TABLE I

$n E_{sw}$ mV	$W_{1/2}, \psi^+$				$\Delta\psi_{max}^+$	$W_{1/2}, \psi^-$				$\Delta\psi_{max}^-$
	Front Side mV	Back Side mV	Total Width mV	Peak Potential mV vs $E_{1/2}$		Front Side mV	Back Side mV	Total Width mV	Peak Potential mV vs $E_{1/2}$	
5	45.9	46.7	92.6	-1.5	.1988	45.4	44.7	90.1	-1.8	.2158
10	46.3	46.8	93.1	- .95	.3609	46.2	45.7	91.9	-2.2	.3771
15	47.1	47.5	94.6	- .70	.5166	47.2	46.8	94.0	-2.5	.5315
20	48.3	48.7	97.0	- .58	.6636	48.5	48.2	96.7	-2.6	.6769
30	51.7	52.1	103.8	- .43	.9246	52.1	51.8	103.9	-2.7	.9340
40	56.4	56.7	113.1	- .33	1.137	57.0	56.6	113.6	-2.8	1.143
50	62.2	62.6	124.8	- .26	1.301	62.9	62.5	125.4	-2.9	1.304

Conditions: $n\Delta E = 5$ mV, $\sigma = .5$, $\rho_1 = 0.499$, $\rho_2 = 0.999$

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FIGURE CAPTIONS

- Figure 1. Square wave waveform with associated nomenclature, τ is the step width for the base staircase.
- Figure 2. Individual and difference current functions for three square wave amplitudes. $n\Delta E = 5$ mV, $\sigma = 0.5$, $\rho_1 = 0.499$, $\rho_2 = 0.999$
- (A) $nE_{sw} = 5$ mV
- (B) $nE_{sw} = 15$ mV
- (C) $nE_{sw} = 30$ mV
- Solid line is difference current function, $\Delta\psi^+$
- Figure 3. Individual and difference current functions at the peak ($\Delta\psi_{max}^+$) vs square wave amplitude. $n\Delta E = 5$ mV, $\sigma = 0.5$, $\rho_1 = 0.499$, $\rho_2 = 0.999$.
- (■) $\Delta\psi_{max}^+$
- (●) ψ_f at peak
- (▲) ψ_r at peak
- Figure 4. Peak width at half height vs square wave amplitude. $n\Delta E = 5$ mV, $\sigma = 0.5$, $\rho_1 = 0.499$, $\rho_2 = 0.999$.
- Figure 5. Individual forward and reverse current functions as a function of ΔE . $nE_{sw} = 20$ mV, $\sigma = 0.5$, $\rho_1 = .499$, $\rho_2 = .999$
- (A) $n\Delta E = 10$ mV
- (B) $n\Delta E = 5$ mV
- (C) $n\Delta E = 2$ mV
- (D) $n\Delta E = 1$ mV
- Figure 6. Effect of measurement time on $\Delta\psi^+$. $n\Delta E = 5$ mV, $nE_{sw} = 20$ mV, $\sigma = 0.5$, $\rho_2 = \sigma + \rho_1$
- (A) $\rho_1 = .05$
- (B) $\rho_1 = 0.1$
- (C) $\rho_1 = 0.3$
- (D) $\rho_1 = 0.499$

Figure 7. Peak current function, $\Delta\psi_{\max}^+$, vs σ . $n\Delta E = 5$ mV, $nE_{\text{sw}} = 20$ mV.

(◆) $\rho_1 = \sigma - 0.001$, $\rho_2 = 0.999$

(▲) $\rho_1 = 0.049$, $\rho_2 = \sigma + 0.049$

Figure 8. Effect of asymmetric measurements on asymmetric square waves.

$n\Delta E = 5$ mV, $nE_{\text{sw}} = 20$ mV, $\rho_1 = \sigma - 0.001$, $\rho_2 = 0.999$.

(A) $\sigma = 0.1$

(B) $\sigma = 0.5$

(C) $\sigma = 0.9$

Symmetry of waveform shown in inset, (x) indicates current measurement.

Figure 9. Effect of asymmetric measurements on asymmetric square waves.

$\rho_1 = 0.049$, $\rho_2 = \sigma + 0.049$, other conditions and legend same as Figure 8.

Figure 10. Change in current function with sampling time $n\Delta E = 5$ mV,

$nE_{\text{sw}} = 20$ mV, $\sigma = 0.1$, $\rho_1 = 0.099$

(A) $\rho_2 = 0.149$

(B) $\rho_2 = 0.999$

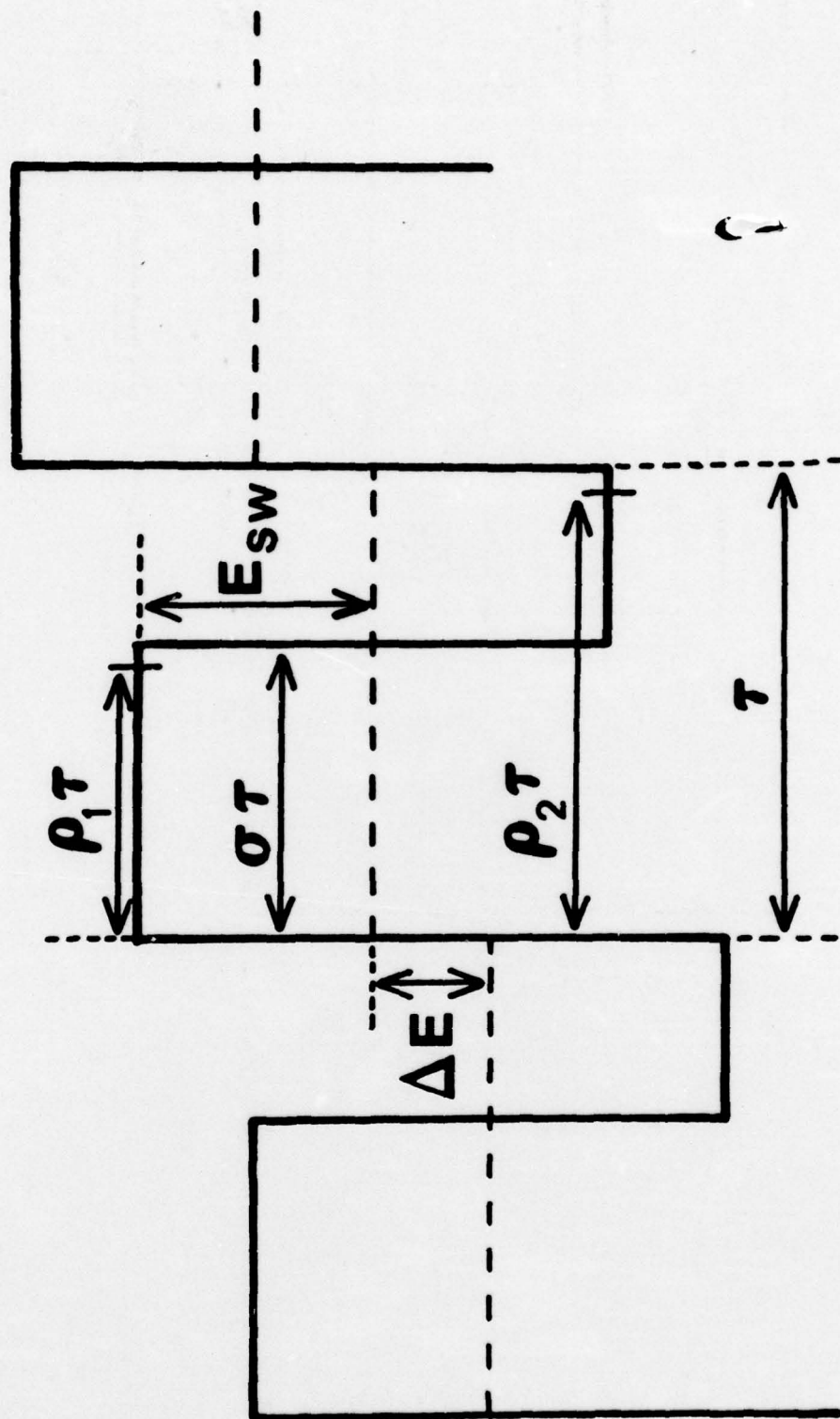


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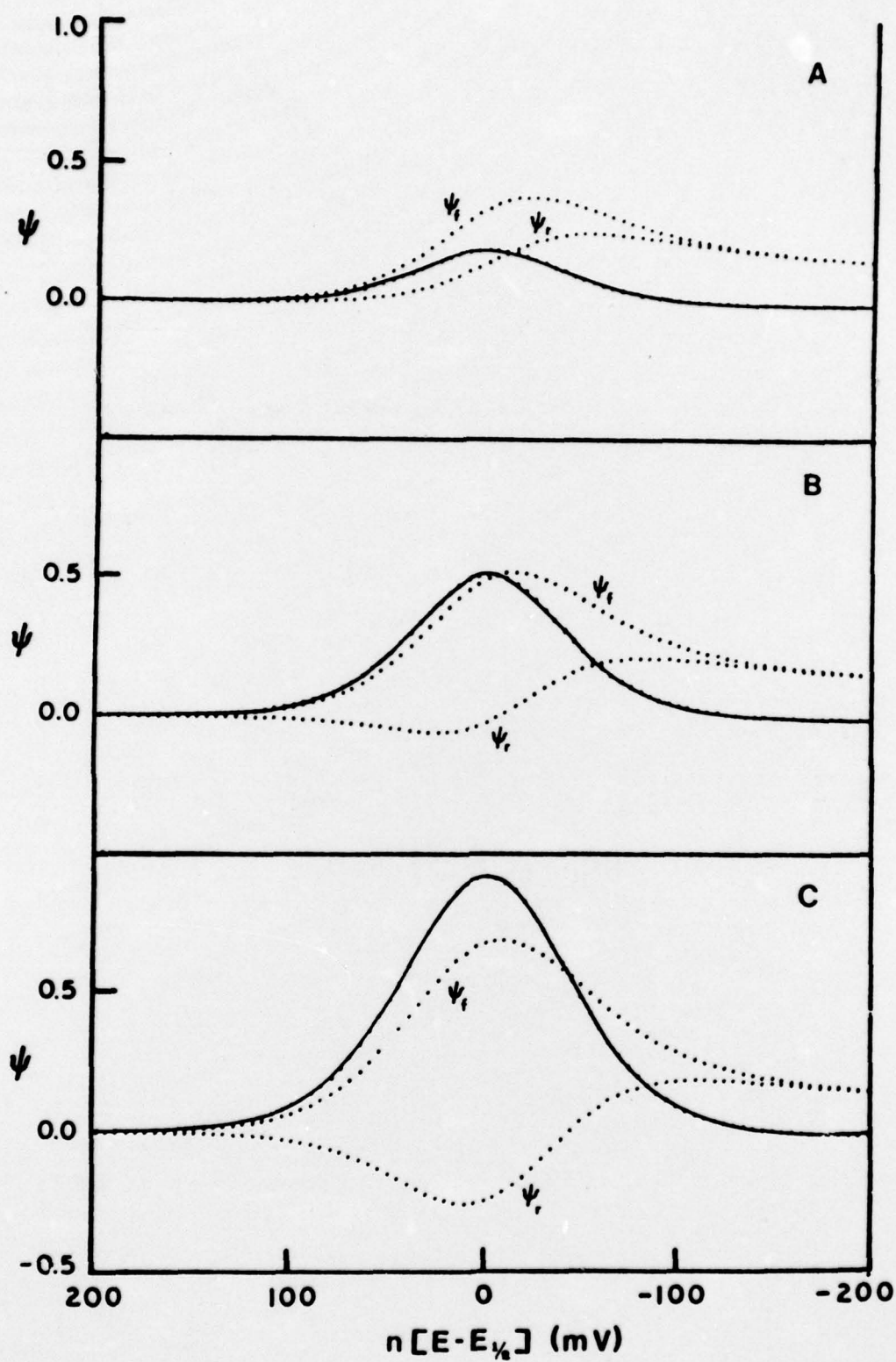


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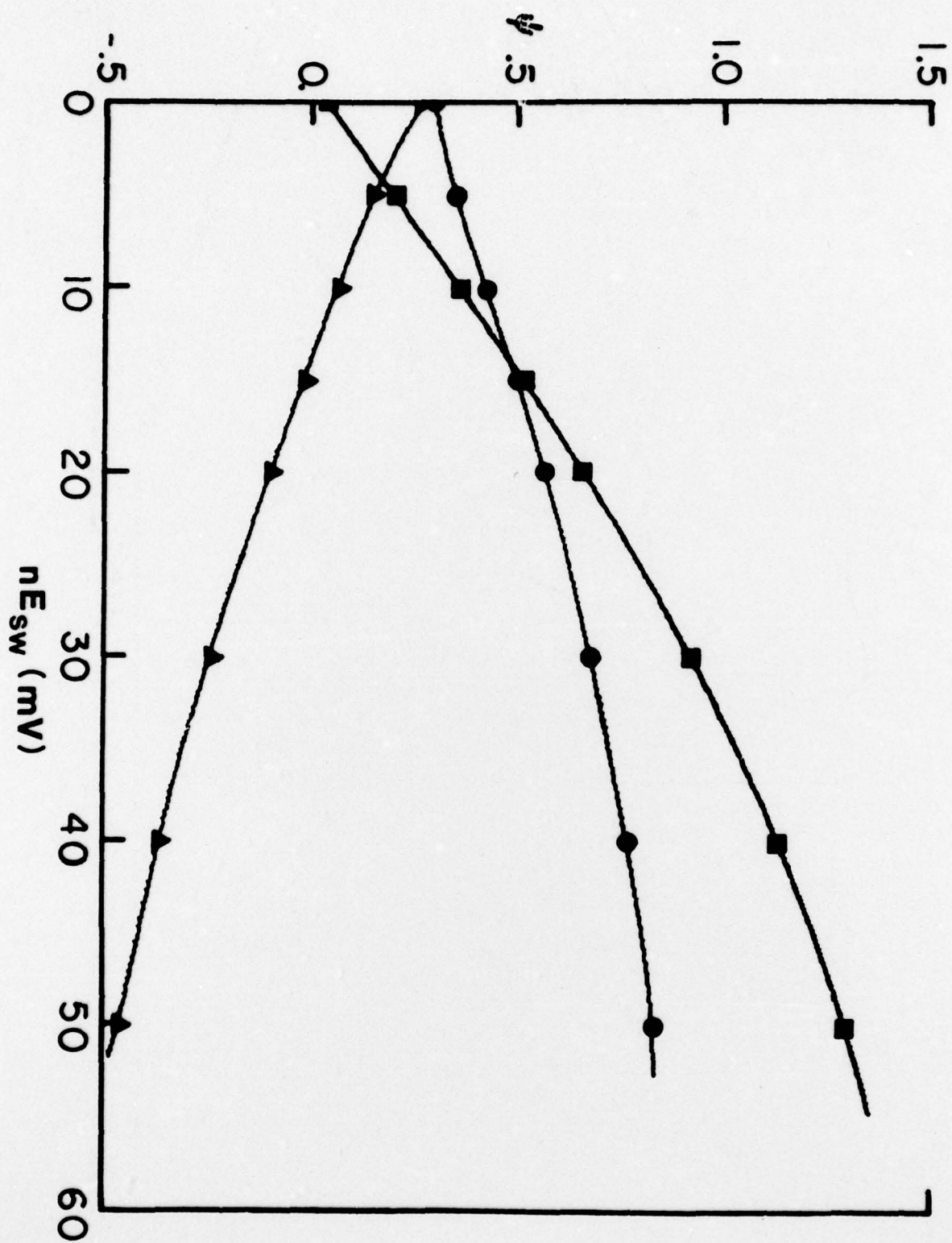


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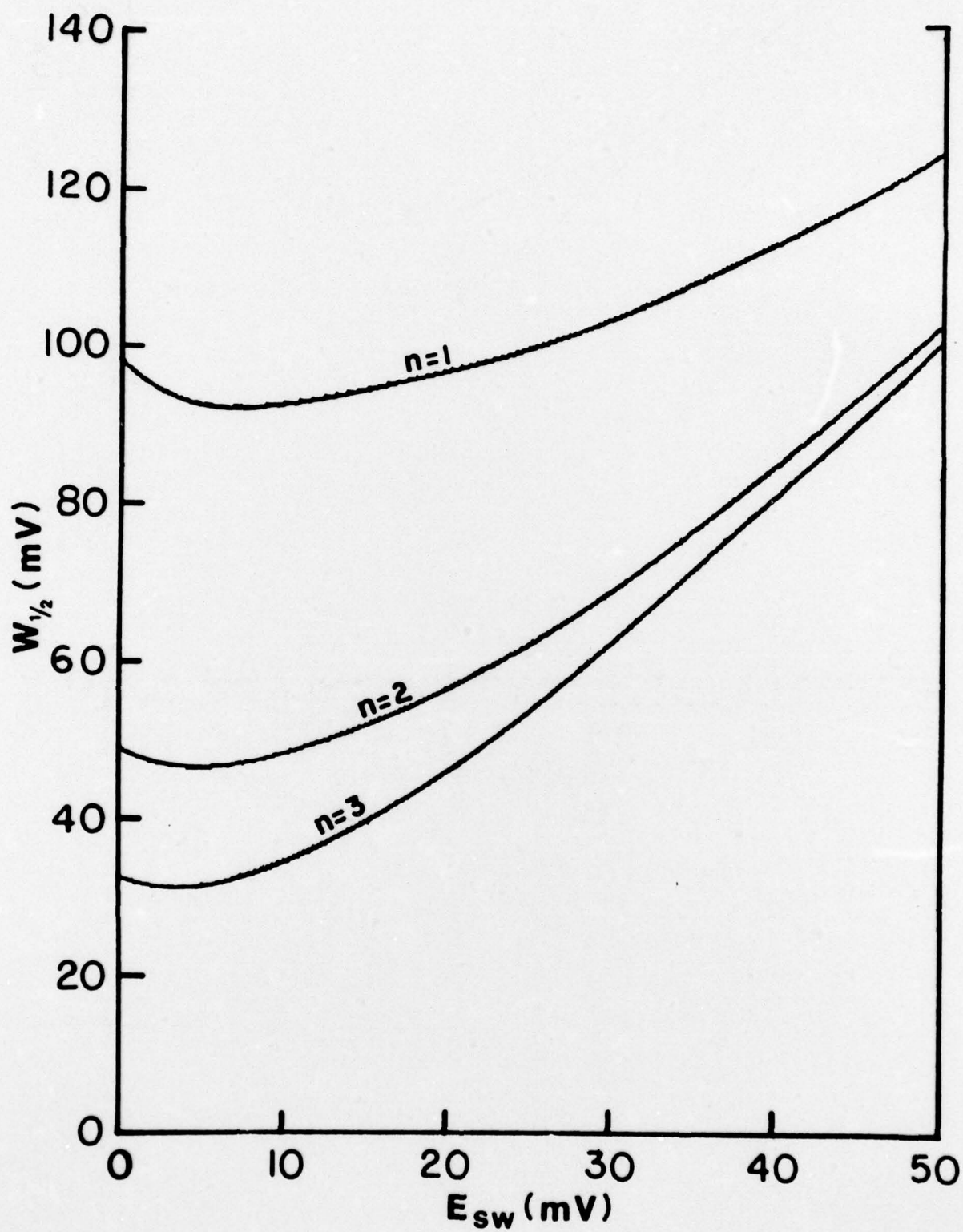


Figure 4

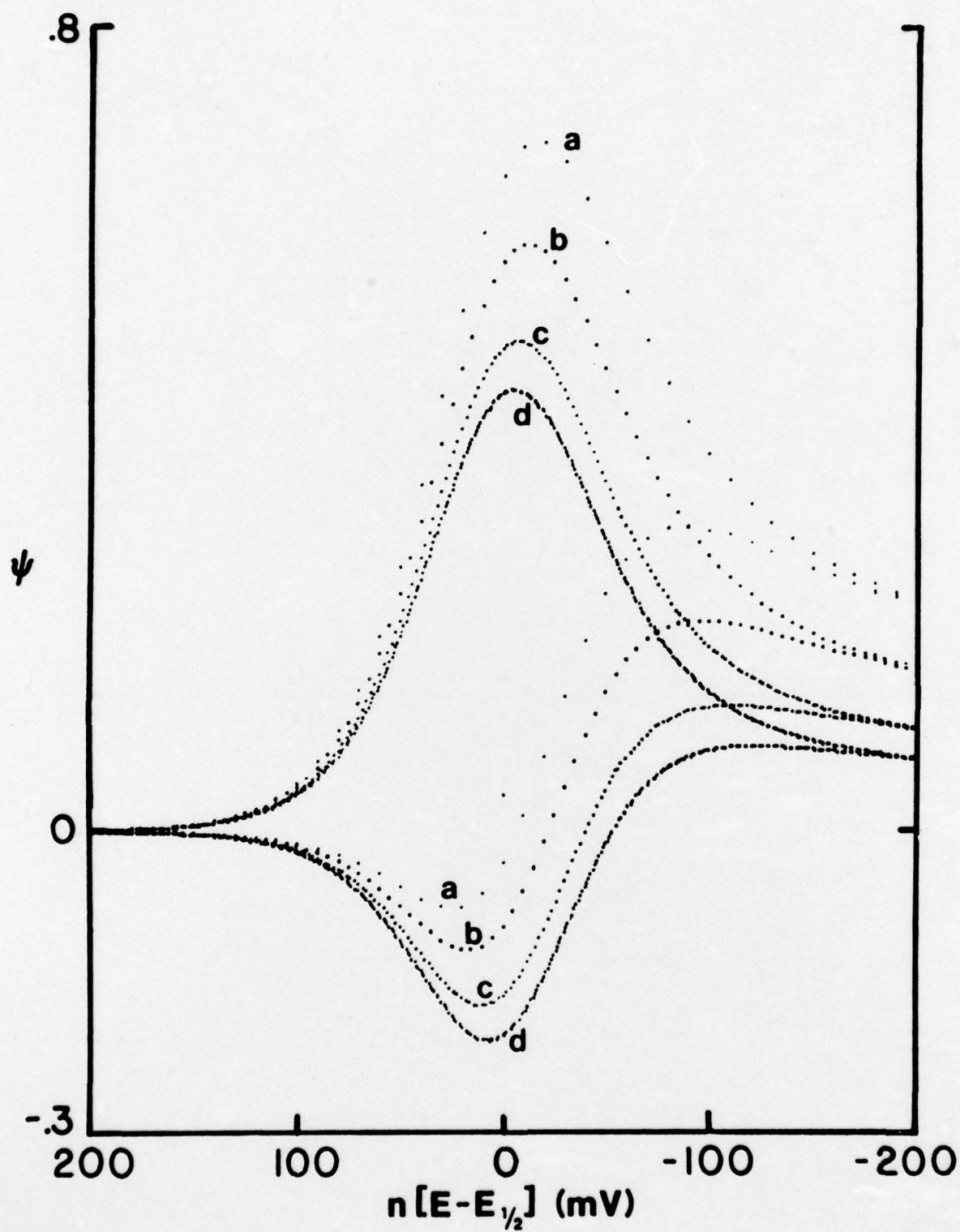


Figure 5

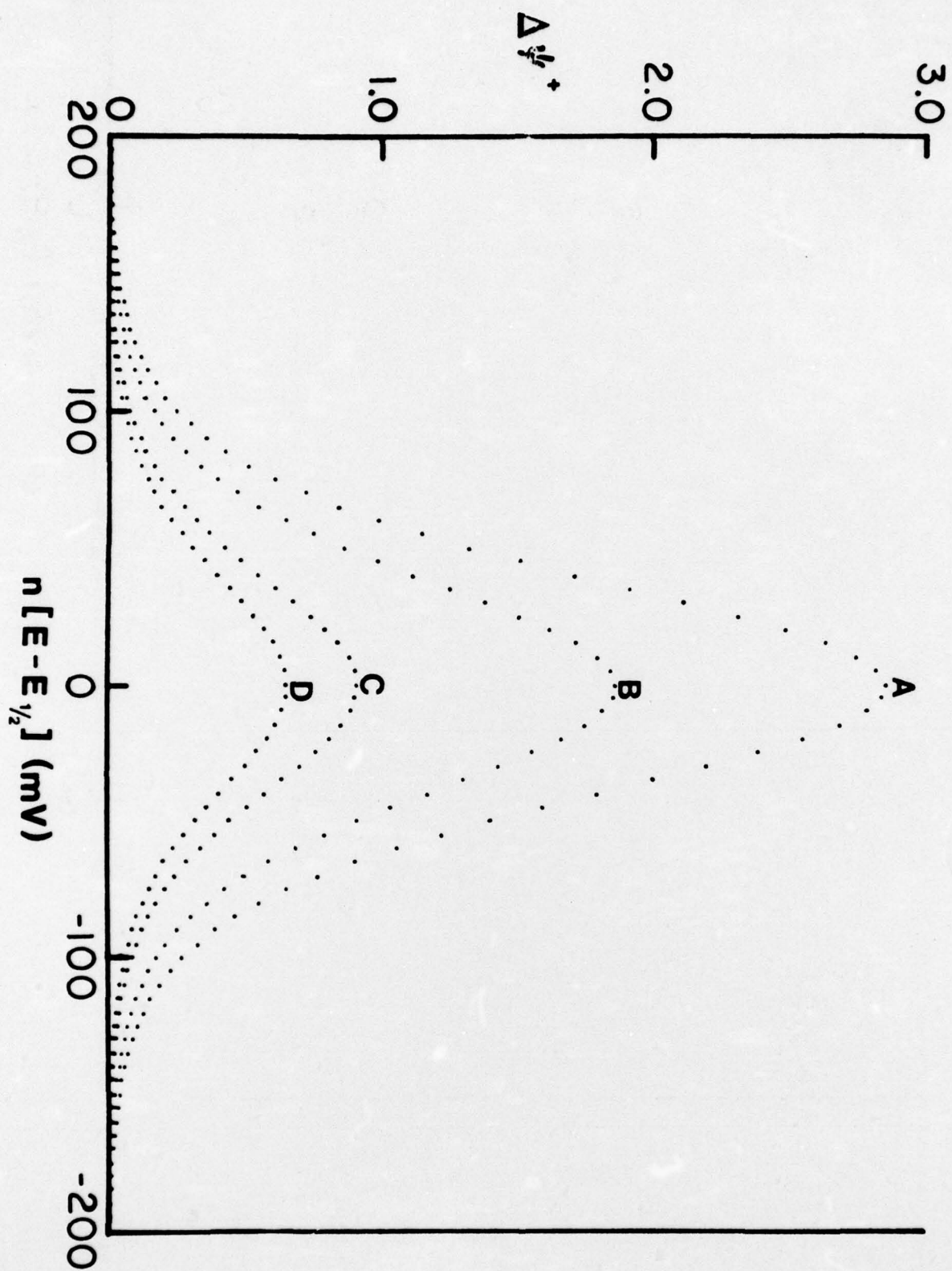


Figure 6

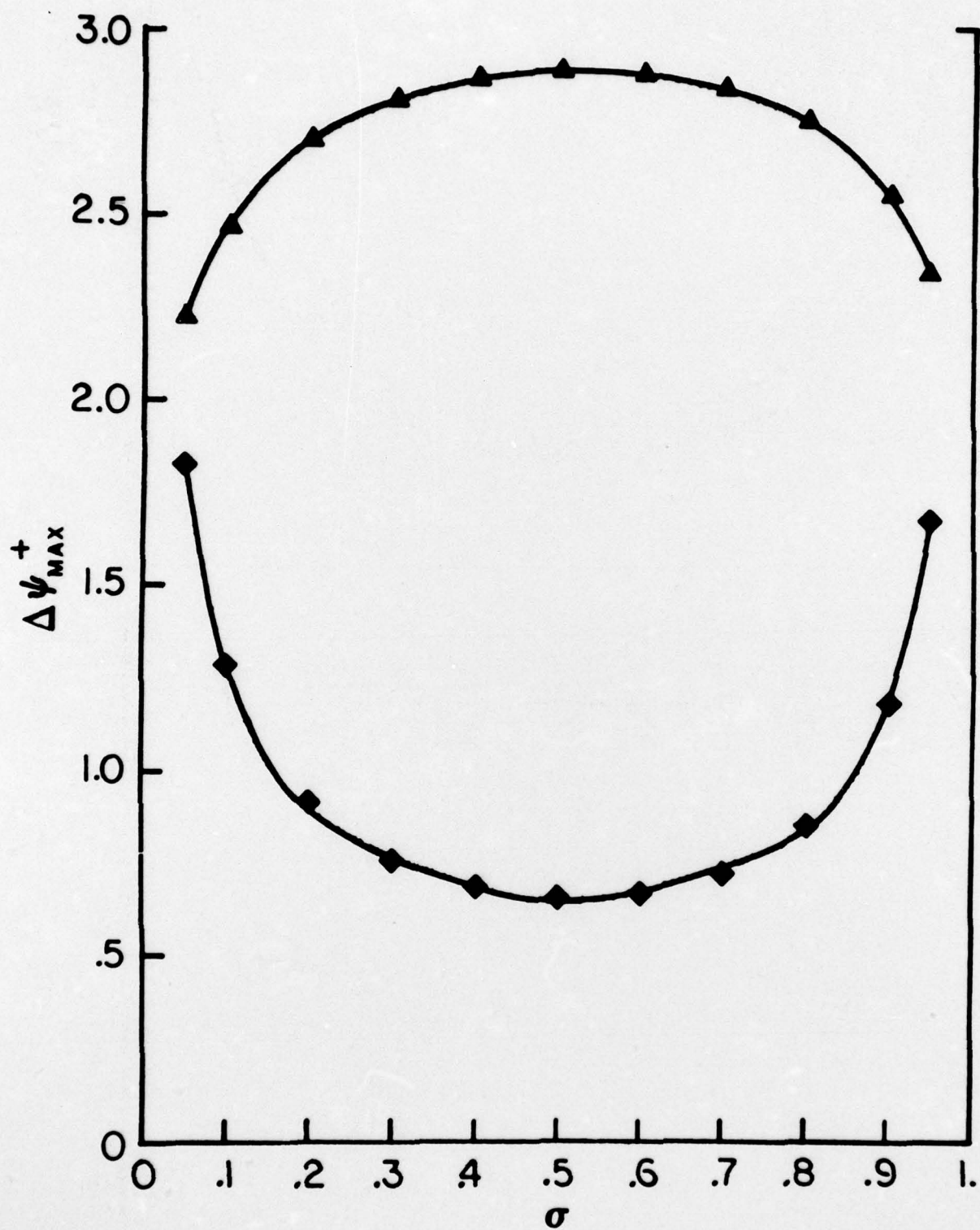


Figure 7

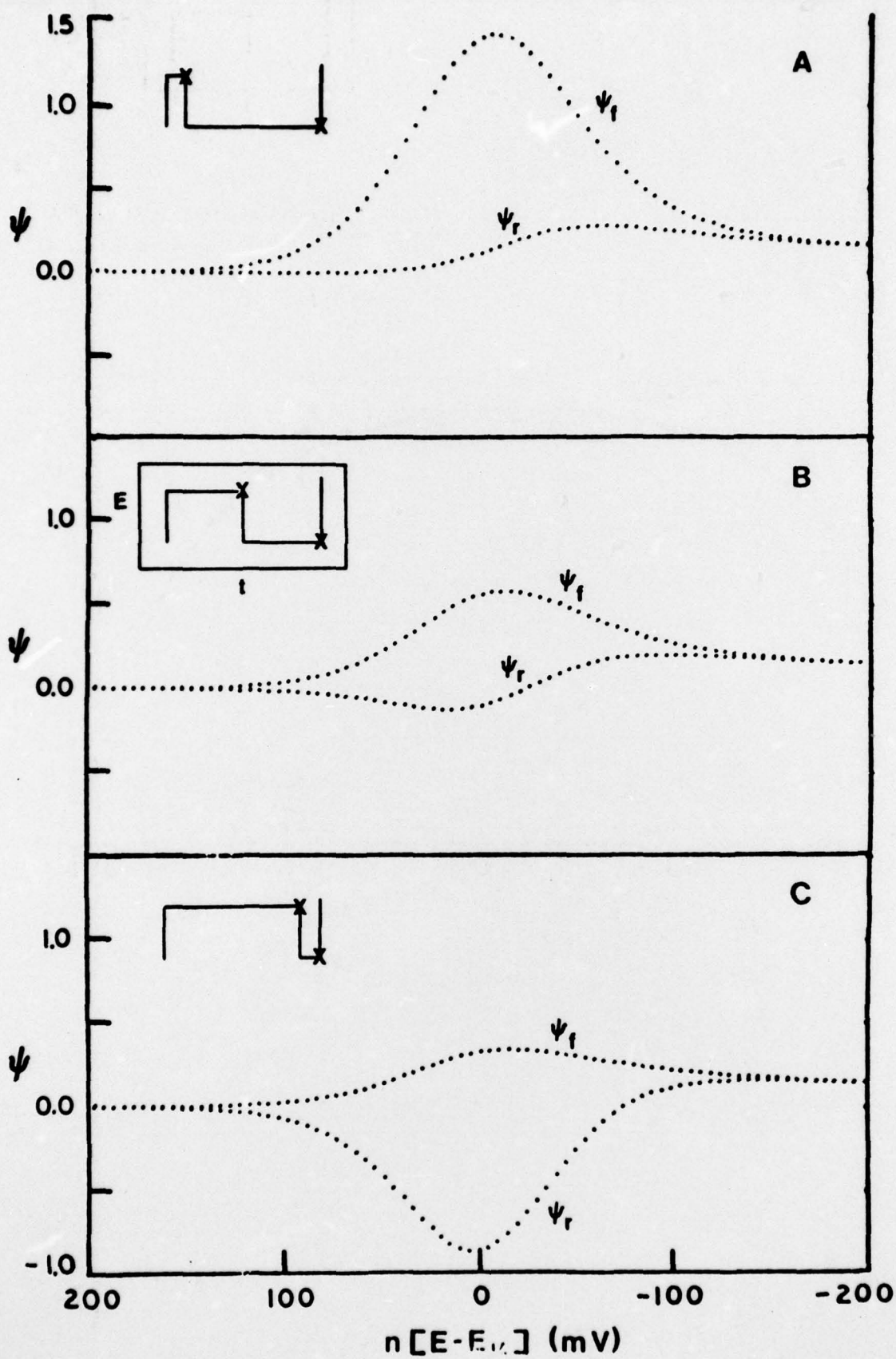


Figure 8

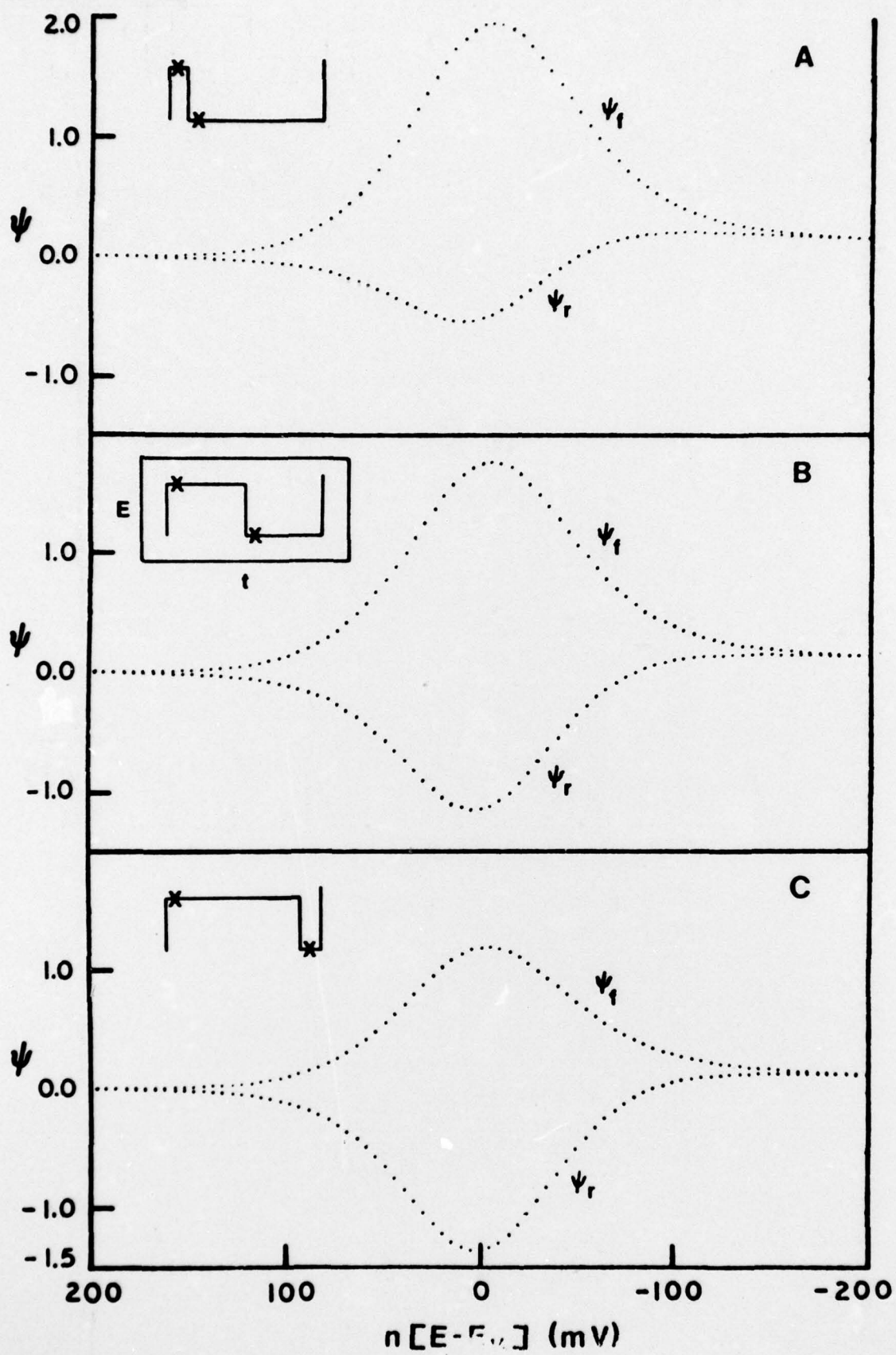


Figure 9

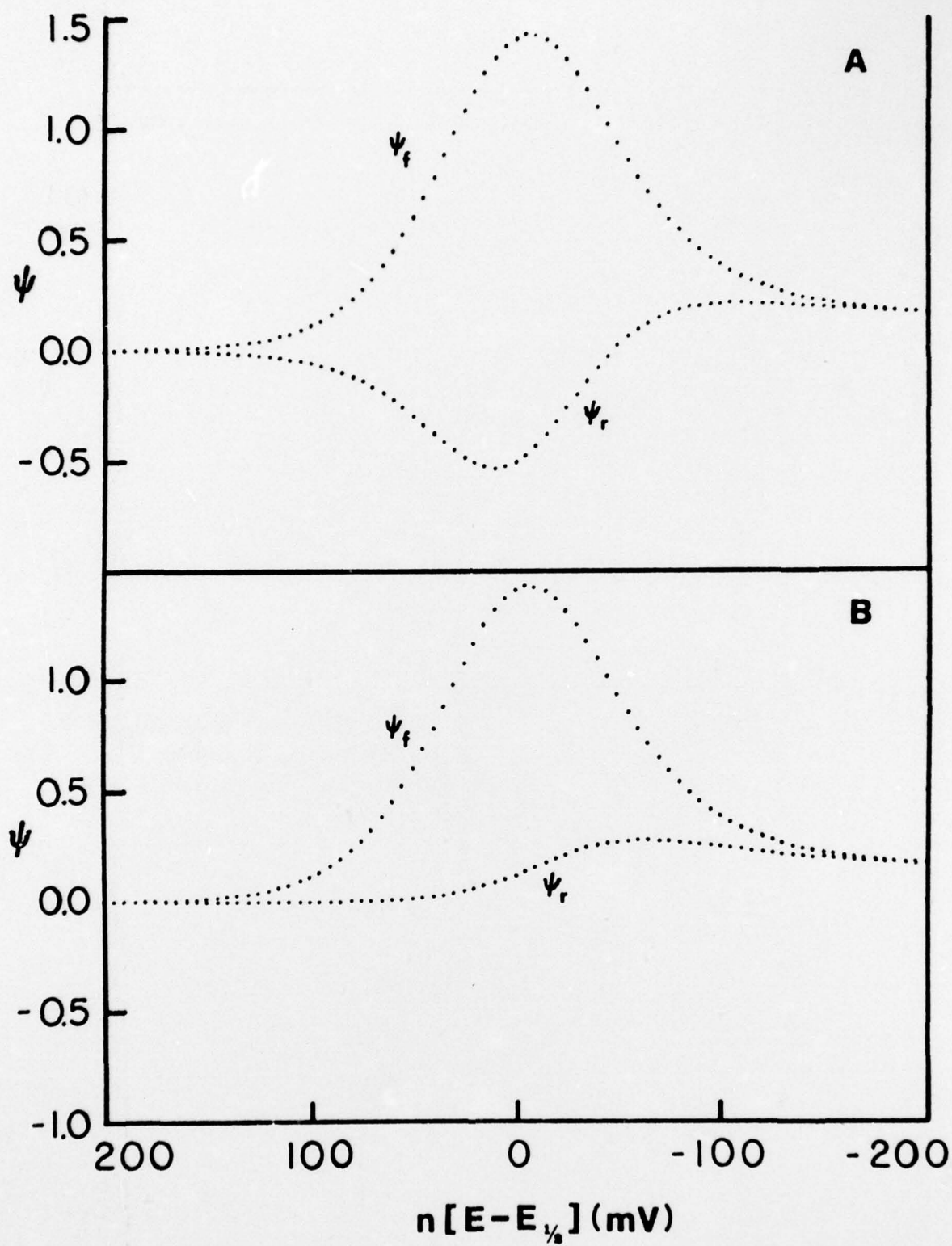


Figure 10

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