Wide-band approximation in the theories of charge transfer during ion-surface scattering

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(Received 24 May 1993; revised manuscript received 18 October 1993)

The validity of the wide-band approximation is discussed and, in particular, the effects of the speed of the ion and the position of ion orbital energy relative to the band are considered. It is shown that care is needed in interpreting the integrals involved using generalized functions and that, for slow ions and a wide band, the wide-band approximation is valid for orbital energies well within the band, partially valid at the band edges, and invalid outside the band. Equations are also derived for mixed bands including the situation where the band can be divided into two parts, a narrow band and a wide band.

I. INTRODUCTION

There has been much recent interest in the mechanisms involved in the neutralization of ions scattered from solid surfaces. The predominant processes are resonant charge transfer (RCT) and Auger charge transfer. In theoretical studies of both of these, when the participating energy band of the solid is wide considerable simplifications can be obtained using the wide-band approximation (WBA).[1-5] However, the validity of the approximation has not been widely discussed, although see the review article by Brako and Newns[3] and Refs. 1 and 2. Also relevant are the papers by Sulston, Amos, and Davison[6] who used the WBA in the case where the surface density of states (SDOS) has a semielliptical form to illustrate how the behavior of the final neutralization probability depends on the bandwidth and the interaction strength and by Tsuneyuki, Shima, and Tsukada[5] who considered the effect of the bandwidth for different types of SDOS.

Essentially the WBA involves an approximation of the inverse Fourier transform of a SDOS by a δ function and, by implication and assumption, the width of the band, rather than its structure, is the important feature. Indeed, the archetypal WBA can be considered as derived for a band with a uniform density. In this note, we use the theory of generalized functions to discuss other band structures which lead to a WBA equivalent to that found for a uniform band density. In addition, we examine what effect the position of the energy of the ion, relative to the band, has on the effectiveness of the WBA. We find that for satisfactory results the ion energy and the band energies must be in resonance and that WBA should not be used in quasiresonance calculations.

Since our main objective is to investigate the WBA rather than consider RCT in general terms, we have chosen to illustrate the theory with a simple set of coupled differential equations from the many-electron theory (MET) of RCT.[7-9] Although this corresponds to the most elementary theoretical model of RCT the ideas can be readily applied in other situations including the theory of Auger charge transfer.[10] In Appendixes A and B we briefly discuss the effect of more elaborate models on our analysis of WBA. We find that, with minor adaptions, the discussion of the validity of WBA remains essentially unchanged for these more sophisticated models.

II. PRELIMINARIES

The simplest model of RCT describes a situation in which an ion with a completely vacant valence orbital u_0 approaches a surface and interacts with a band in the solid with n band orbitals $\{\phi_k, k=1,\ldots,n\}$, each doubly occupied by electrons with opposite spins. Using the MET, the initial state, with the ion far from the surface, is

$$\Psi_0=|\phi_1(1)\bar{\phi}_1(2)\cdots\phi_n(2n-1)\bar{\phi}_n(2n)|\ , \tag{1}$$

where bar (no bar) indicates α (β) spin. When the ion is near the surface, the interaction between the ion and surface can cause an electron to transfer from a band orbital to u_0. If Ψ_k is the singly excited configuration describing this transfer from ϕ_k or $\bar{\phi}_k$ and we write the time-dependent wave function for the system as

$$\Psi=\left\{a_0\Psi_0+\sum_{k=1}^{n} b_k\Psi_k\right\}\exp -iE_0t \tag{2}$$

with E_0 the energy of (1), then the equations satisfied by the time-dependent coefficients are

$$\begin{aligned} i\frac{da_0}{dt}&=\sqrt{2}V(t)\sum_{k=1}^{n} v_k b_k\ , \\ i\frac{db_k}{dt}&=(e_0-e_k)b_k+\sqrt{2}v_kV(t)a_0,\quad k=1,2,\ldots,n\ . \end{aligned} \tag{3}$$

This set of first-order linear differential equations has to be solved subject to the initial conditions $a_0(-\infty)=1$ and $b_k(-\infty)=0$. In deriving (2), the interaction potential V is assumed to have matrix elements

$$\langle\phi_k|Vu_0\rangle=v_kV(t)\ , \tag{4}$$

where we have chosen ϕ_k real so that the v_k are real constants independent of time. The parameters e_0 and e_k are the orbital energies of u_0 and ϕ_k, respectively, and we take the center of the band as the energy origin. Strictly, u_0 and, hence, e_0 will depend on time, but, for simplification, we treat e_0 as a constant equal to its average value during the time when the ion-surface interaction is strong. This simplification does not affect the analysis of the applicability of the WBA and the more general case is discussed in Appendix A. Also, in our model, the wave function (2) does not contain configurations which allow for an electron to move back from the atom into an originally unoccupied orbital with an energy above the Fermi level. The effect of including such a configuration is discussed in Appendix B.

Integrating the equations for $\{b_k\}$ and substituting leads to

$$\frac{da_0}{dt}=-2V(t)\int_{-\infty}^{t}a_0(u)V(u)\times\sum_{k=1}^{n}v_k^2\exp\{i(e_k-e_0)(t-u)\}du\ . \tag{5}$$

For a dense band we may replace the sum over k by an integral. Essentially

$$v_k^2\approx\rho(e_k)\Delta y_k,\quad \Delta y_k=e_{k+1}-e_k \tag{6}$$

so that

$$\frac{da_0}{dt}=-2V(t)\int_{-\infty}^{t}a_0(u)\times V(u)\left[\int_{-\beta}^{\beta}\rho(y)\exp\{i(t-u)y\}dy\right]\times\exp\{ie_0(u-t)\}du\ . \tag{7}$$

Here $\rho(y)$ is the SDOS referred to an origin, $y=0$, at the center of the band, the bandwidth is 2β and ρ satisfies the normalization condition

$$\int_{-\beta}^{\beta}\rho(y)dy=1\ . \tag{8}$$

Essentially for the WBA we replace

$$\int_{-\beta}^{\beta}\rho(y)\exp i(t-u)ydy \tag{9}$$

by $\pi\beta^{-1}\delta(t-u)$ so that (7) becomes

$$\frac{da_0}{dt}=-\pi\mu\frac{V^2(t)}{\beta}a_0\ . \tag{10}$$

In Eqs. (7) and (10) it is assumed that $\sum v_k^2=1$. If this condition is not satisfied then μ should be multiplied by the factor $\sum v_k^2$. Apart from this the constant μ in (10) has to be chosen to take into account the range of integration over u in (7), which is from $-\infty$ to t rather than $-\infty$ to ∞, and to allow for the effect of the position of e_0 which affects the approximation through the factor $\exp ie_0(u-t)$ in (7). This is discussed in Sec. IV of this paper where we consider the validity of the WBA.

Since $a_0(-\infty)=1$ we can integrate (10) to obtain

$$a_0=\exp\left\{-\mu\int_{-\infty}^{t}\frac{\pi V^2(x)}{\beta}dx\right\} \tag{11}$$

so that the probability of electron transfer and ion neutralization is

$$P=1-|a_0|^2=1-\exp\left\{-2\mu_R\int_{-\infty}^{\infty}\frac{\pi V^2(x)}{\beta}dx\right\}, \tag{12}$$

where μ_R is the real part of μ. As this last point implies, there are some circumstances when the constant μ is complex but P, the quantity of physical interest, depends only on the real part of μ. This is because the imaginary part of μ gives rise to a phase factor for a_0 which can be allowed for as a perturbation of e_0 and in turn causes a perturbation in the value of μ_R. Thus there is no loss of generality if, when μ is complex, we replace it in (10) and (11) by its real part (see, also, Sec. VI).

For $\beta\gg\int_{-\infty}^{\infty}V^2(x)dx$, we have $P\approx0$ and negligible probability of electron transfer. In the opposite situation, for $\beta\ll\int_{-\infty}^{\infty}V^2(x)dx$, we have $P\approx1$, so that for large interaction strengths electron transfer is guaranteed. These conclusions are in line with the numerical results found from direct integration of Eq. (2) for a semielliptical SDOS (Ref. 5) but they do not rely on any particular choice of SDOS. Rather, they constitute a generic property for a class of SDOS. To examine the properties of this class we need to consider the theory of generalized functions. This is done in the next section where it is shown that, for large β, the behavior is the same as for a uniform band.

III. THEORETICAL BACKGROUND ON GENERALIZED FUNCTIONS

In this section we review the theory of generalized functions and the main theorems which are useful for the WBA. This theory follows closely the development given by Lighthill,[11] which in turn relies on the earlier work of Temple[12] and Schwartz.[13] More recently, the theory has been considered by Burrows and Colwell[14] in the context of its pedagogical aspects.

Following Lighthill, we define a good function to be one which is everywhere differentiable any number of times and is such that it, and all of its derivatives, are $O(|x|^{-N})$ as $|x|\to\infty$ for all N. Also, a regular sequence of good functions $\{f_n(x)\}$ is one for which, for any good function $F(x)$, the limit

$$\lim_{n\to\infty}\int_{-\infty}^{\infty}f_n(x)F(x)dx \tag{13}$$

exists. Given these preliminary definitions, the definition of a generalized function can be constructed: A generalized function $f(x)$ is a regular sequence $\{f_n(x)\}$ of good functions, and two generalized functions are said to be equal if the corresponding regular sequences are equivalent, in the sense that they give the same limit in (13). Then, for any good function $F(x)$, the integral

$$\int_{-\infty}^{\infty}f(x)F(x)dx \tag{14}$$

can be defined as the limit in (13).

Some further definitions are required. The first of these is that the Fourier transform, $g(y)$ (say), of a generalized function $f(x)$ is defined to be the sequence $\{g_n(y)\}$ where $g_n(y)$ is the Fourier transform of $f_n(x)$. A similar definition holds for the inverse Fourier transform.

In illustrating how this applies to the WBA, it is simpler, initially, if we restrict the discussion to SDOS which are symmetrical about the band center. Later, in Sec. VI we show how nonsymmetrical SDOS can be treated. In the context of generalized functions, we point out that the regular sequences of good functions associated with symmetrical SDOS will consist of even functions only. Let us write the SDOS in the form

$$\rho(\beta,y)=\frac{1}{2\beta}g(\beta,y) \tag{15}$$

so as to emphasize its dependence on bandwidth, and consider the special case of a uniform SDOS so that

$$g(\beta,g)=g_1(\beta,y)=\begin{cases}1, & |y|\leq\beta\\ 0 & \text{otherwise}\end{cases}. \tag{16}$$

We have for any good function $F(y)$

$$\lim_{\beta\to\infty}\int_{-\infty}^{\infty}g_1(\beta,y)F(y)dy=\int_{-\infty}^{\infty}F(y)dy\ . \tag{17}$$

Now the sequence $\{\exp-(y^2/n^2)\}$ is a regular sequence for 1, so that 1 is a generalized function and we can conclude that

$$\lim_{\beta\to\infty}g_1(\beta,y)=1 \tag{18}$$

in the sense that they are equivalent generalized functions. Taking inverse Fourier transforms we obtain

$$\lim_{\beta\to\infty}\frac{\sin\beta x}{\pi x}=\delta(x)\ . \tag{19}$$

However, the choice of a uniform SDOS is not necessary to produce $\delta(t)$. Consider as an alternative the Gaussian SDOS

$$g_2(\beta,y)=A(\beta)\exp\{-\pi y^2/4\beta^2\}\ , \tag{20}$$

where

$$A(\beta)=2\beta\left[\int_{-\beta}^{\beta}\exp\{-\pi y^2/4\beta^2\}dy\right]^{-1}.$$

Since $\lim_{\beta\to\infty}A(\beta)=1$ we have the generalized function limit

$$\lim_{\beta\to\infty}g_2(\beta,y)=1\ . \tag{21}$$

Taking inverse Fourier transforms

$$\lim_{\beta\to\infty}\left[A(\beta)\frac{\beta}{\pi}\exp(-x^2\beta^2/\pi)\right]=\delta(x)\ . \tag{22}$$

Clearly this means that the structure of the band need not be uniform.

As a third example we can consider the triangular function

$$g_3(\beta,y)=(1-|y|/2\beta)[u(y+2\beta)-u(y-2\beta)]\ , \tag{23}$$

where $u(y)$ is the Heaviside function. The corresponding inverse transform result is

$$\lim_{\beta\to\infty}\frac{1}{\pi}\frac{\sin^2(\beta x)}{\beta x^2}=\delta(x)\ . \tag{24}$$

Thus comparing (19) and (24) we see that $g_3(\beta,y)$ can be approximated closely by $g_1(\beta,y)$ for large β although the bandwidth of the former is 4β rather than 2β, the bandwidth for $g_1(\beta,y)$.

A fourth example is the even function which is 1 in the interval $[0,(k-1)\beta]$, where $k>1$, goes linearly from 1 to 0 in $[(k-1)\beta,(k+1)\beta]$ and is 0 for $t>(k+1)\beta$. This leads to the result

$$\lim_{\beta\to\infty}\frac{1}{\pi}\frac{\sin(\beta x)\sin(k\beta x)}{\beta x^2}=\delta(x)\ . \tag{25}$$

For $0<k<1$ the equivalent result is $k\delta(x)$.

These last examples illustrate that for the WBA we do not need the symmetric SDOS to be uniform but only to possess the property that, when regarded as a generalized function, $g(\beta,y)$ satisfies the analogue of (18). This implies that any such symmetrical SDOS can be approximated by a uniform density for sufficiently large β, and that the validity of the WBA can be determined by considering a uniform SDOS and $g_1(\beta,y)$.

IV. THE VALIDITY OF THE WIDE-BAND APPROXIMATION

Writing the SDOS as in (18) and using the inverse Fourier transform we have

$$\frac{1}{2\beta}\int_{-\infty}^{\infty}g(\beta,y)\exp(iyt)dy=\frac{1}{2\beta}\int_{-\beta}^{\beta}g(\beta,y)\exp(iyt)dy=\frac{\pi}{\beta}f(\beta,t) \tag{26}$$

so that (7) becomes, after a change of variable $s=u-t$ in the integral,

$$\frac{da_0}{dt}=-2V(t)\int_{-\infty}^{0}a_0(t+s)V(t+s)\times\pi\beta^{-1}f(\beta,s)\exp(ie_0s)ds\ , \tag{27}$$

where we have used the fact that for the symmetric SDOS we are considering at present, $f(\beta,s)$ is a real even function. In the WBA it is used as a member of a sequence for $\delta(s)$ but it is not enough simply to replace $f(\beta,s)$ by the δ function; some care must be taken in evaluating the resulting integral. We now consider three aspects of this: (a) the role played by the limits of integration in (27); (b) the effect of the position of e_0, which affects the approximation through the exponential factor in the integral in (27); (c) the significance of the velocity of the ion which partly determines the range of $V(t)$. The last two points are related to the question of how far we can take the $\beta\to\infty$ limit for $f(\beta,s)$ independently of the remaining terms in the integrand.

Firstly considering the range of integration for the integral on the right-hand side of (27), it might be thought that, having replaced $f(\beta,s)$ by the δ function, the in-

tegral could be treated as if the limits corresponded to the full range $(-\infty,\infty)$ so giving (10) with $\mu=2$. We wish to argue that this procedure is incorrect. In principle, the integral of $\delta(s)$ with respect to s from $-\infty$ to 0 is undefined since the value obtained depends on the sequence used. However, $f(\beta,s)$ is an even function of s as are the other functions considered in the preceding section so that the sequences associated with symmetric SDOS in the WBA are even functions. This is an important factor and to emphasize it let us denote the δ function obtained from such sequences as $\delta^+(s)$. The approximation to be invoked is that in these circumstances the integral from $-\infty$ to 0 is one-half the integral from $-\infty$ to ∞, so that

$$\int_{-\infty}^{0}\delta^+(s)F(s)ds=\tfrac{1}{2}F(0) \tag{28}$$

for good functions $F(s)$. The consistency of this approximation is now discussed.

We consider a sequence for $\delta(x)$ consisting of even functions $\{p_n(x)\}$ such that

$$\int_{-\infty}^{0}p_n(x)dx=\tfrac{1}{2} \tag{29}$$

and

$$\lim_{n\to\infty}\int_{-\infty}^{0}g(x)p_n(x)dx=0 \tag{30}$$

for any good function $g(x)$ for which $g(0)=0$. An example of such a sequence is

$$p_n(x)=\left[\frac{n}{\pi}\right]^{1/2}\exp(-x^2n^2) \tag{31}$$

and all the examples of $f(n,x)$ considered in Sec. III are of this form. Using Taylor's theorem with any good function $F(x)$, we have

$$F(x)=F(0)+xF'(v) \tag{32}$$

for some v between x and 0. Since $F(x)$ is a good function, it follows that

$$\int_{-\infty}^{0}F(x)p_n(x)dx=F(0)\int_{-\infty}^{0}p_n(x)dx+\int_{-\infty}^{0}F'(v)xp_n(x)dx\ . \tag{33}$$

The first term on the right-hand side of (33) is just $\frac{1}{2}F(0)$ and, letting $n\to\infty$, the second vanishes by (30), so giving (28). Unfortunately, this is not quite sufficient to deal with (27) since other terms in the integrand may have some β dependence; this is equivalent in the above analysis to having $F(x)$ dependent on the limit $n\to\infty$. Even in such a case, (32) and (33) still hold but (30) may not when $g(x)=xF'(v)$ so the second integral in (33) may not be zero. Essentially we need to assume that $F(x)$ remains a good function for all n.

When these results are applied to (27), it is consistent to replace $f(\beta,s)$ by $\delta^+(s)$ and to use (28) provided the remaining functions comprising the integrand are good functions with derivatives of order β^{-1}. Because the variable for a_0 and V in (27) is $t+s$, this is equivalent to assuming that their product is slowly varying over *any* interval $O(\beta^{-1})$, while the exponential involving e_0 is unimportant when e_0 has no β dependence. The first condition should hold for slow ions and the second when e_0 is in resonance with the band. When both of these are the case we obtain (10) with $\mu=1$.

Indeed, this result will hold even if we do not take the $\beta\to\infty$ limit. Suppose β is large but not infinite. The function $f(\beta,s)$ can be neglected, i.e., set to zero, outside the interval $[-n\beta^{-1},0]$ with $n\approx 5$–6, so that the lower limit of $-\infty$ in the integral on the right-hand side of (27) can be replaced by $-n\beta^{-1}$. If $|e_0|\ll\beta$, the exponential term in the integral can be replaced by unity from which value it will change only negligibly in $[-n\beta^{-1},0]$. Similarly, provided the product $a_0(t+s)V(t+s)$ varies only slowly for $-n\beta^{-1}<s<0$, and for all values of t, which is likely to be the case for slow ions, then it can be replaced by $a_0(t)V(t)$ and taken outside the integral (cf. Refs. 3 and 4 and the local time approximation in Ref. 15). There remains only $f(\beta,s)$ in the integral and that can be evaluated to give the one-half factor. Thus under the conditions stated we again obtain (10) with $\mu=1$.

We now turn to the case where e_0 does play a role. This occurs when it lies at a band edge or outside the band so that the condition $|e_0|\ll\beta$ does not hold. To see the consequences of this we write $e_0=k\beta$, apply the inverse Fourier transform with the uniform density of states in (27) and consider

$$\frac{2\pi}{\beta}\int_{-\infty}^{0}\frac{\sin\beta s}{\pi s}\exp\{ik\beta s\}V(t+s)a_0(t+s)ds\ . \tag{34}$$

When the product of a_0 and the interaction potential satisfies the same conditions as before, the large β behavior of the integral will be determined by the first three terms. Combined together they have a real part which is

$$R(\beta,k,s)=\frac{\pi}{\beta}\left[\frac{\sin(1+k)\beta s}{\pi s}+\frac{\sin(1-k)\beta s}{\pi s}\right] \tag{35}$$

and an imaginary part

$$I(\beta,k,s)=2\pi s\left[\frac{\sin(\beta s)\sin(k\beta s)}{\pi\beta s^2}\right]\ . \tag{36}$$

The imaginary part (36) is easy to deal with since by (25) we see that for large β

$$I(\beta,k,s)\approx\pi s\delta^+(s)h(k)\ , \tag{37}$$

where $h(k)=k$ for $|k|<1$ and $\mathrm{sign}(k)$ otherwise.

Consequently, on substituting (37) into (34), it follows that the imaginary part of (34) will be small for large β, tending to zero as $\beta\to\infty$.

The behavior of $R(\beta,k,s)$ is more complicated and for large β depends critically on the size of k. For large β and $|k|\gg 1$ so that e_0 is well out of the band we have

$$R(\beta,k,s)\approx\frac{\pi}{\beta}\{\delta^+(s)-\delta^+(s)\}\approx 0 \tag{38}$$

while for large β and $|k|<1$ so that e_0 is inside the band and we have resonance

$$R(\beta,k,s)\approx\frac{\pi}{\beta}\{\delta^+(s)+\delta^+(s)\}\ . \tag{39}$$

However, for $k\approx 1$ or $k\approx -1$ the value of β needs to be larger for (39) to be invoked. For example, when $k\approx -1$ we need β large enough so that $\{\sin(1+k)\beta s\}/\pi s \approx\delta^+(s)$.

For the special case when $|k|=1$, which corresponds to the ion energy e_0 exactly coinciding with the edge of the band,

$$R(\beta,k,s)\approx\frac{\pi}{\beta}\delta^+(s)\ . \tag{40}$$

In general, therefore, on substituting the appropriate $R(\beta,k,s)$ from (38), (39), or (40) into (34) and (27), we obtain (10) with $\mu=0$ for e_0 well outside the band and $\mu=1$ for e_0 well within the band. With e_0 near a band edge μ can take any value between 0 and 1. This implies that the WBA should not be used for quasiresonance calculations but only where the energy of the ion is in resonance with the band. In principle e_0 depends on time so that, if we can ignore the interaction effects before e_0 reaches resonance with the band, the WBA may be invoked for a large bandwidth 2β. Thus the validity of the WBA usually will not depend on e_0 at $t=\infty$ or $t=-\infty$ but only on its behavior during the time interval where the interaction between ion and surface is strong and the time dependence of e_0 in that interval must be such that it is in resonance with the band for a significant time if the WBA is to produce trustworthy results.

Now we will consider the effect of larger incident velocities, which implies that the ion is close to the surface only for a short time so that the interaction potential $V(t)$ will have large values only for a small time interval around $t=0$. In terms of such commonly used potentials as $\exp-\alpha|t|$ and $\exp-\alpha t^2$, the parameter α will be large and, therefore, around $t=0$ the potential will change rapidly for small changes in t. Thus the condition that $V(t)$ be slowly varying over any interval $O(\beta^{-1})$ will not hold and, in general, the WBA ought not to be used for fast ions. Usually in these circumstances $|a_0(t)|$ exhibits oscillatory behavior which cannot arise in the WBA.

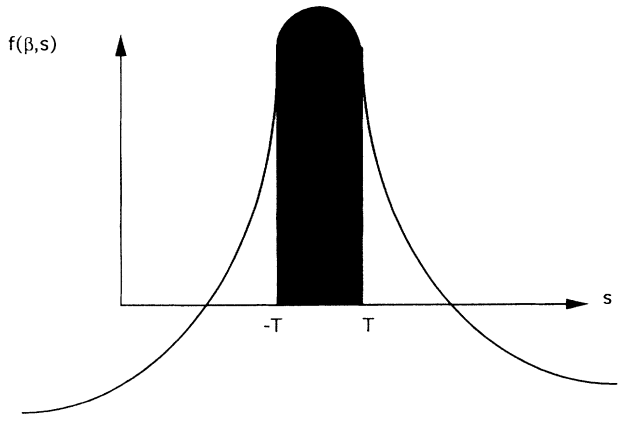

FIG. 1. The significant part of $f(\beta,s)$ in the case of fast ions. For fast ions, the interaction strength is effectively zero outside $|s|<T$ so that the shaded area indicates the only part of $f(\beta,s)$ which is used.

However, there is a rather special case where a form of WBA does hold for fast ions. Suppose the interaction is significant only within the interval $[-T,T]$ and for most of the interval it is constant. This means that $V(t)$ will have a large variation only near the points $-T$ and T. For such a $V(t)$, the lower limit of the integral in (27) is $-(T+t)$. When $T<\beta$, we have that

$$\int_{-T}^{0} f(\beta,s)ds=q<\tfrac{1}{2}\ . \tag{41}$$

Thus $\{f(\beta,s)\}$ is a sequence for $2p\delta^+(s)$ rather than $\delta^+(s)$. This is illustrated in Fig. 1 which shows $f(\beta,s)$ and where the shaded part denotes the area $2q$. If e_0 is small and transient effects due to the large changes in $V(t)$ at the points $-T$ and T can be neglected then we can still invoke the WBA provided we include the extra factor q.

V. A NUMERICAL EXAMPLE

We consider the simple interaction potential

$$V(t)=\begin{cases}\dfrac{V_0}{2T}, & |t|<T\\ 0 \text{ otherwise}\end{cases}\ . \tag{42}$$

For small incident velocities the interaction time $2T$ is large whereas when T is small we have a model for large incident velocities. We take the band to be a uniform band of width at 2β. For consistency of the WBA we need the right-hand sides of (7) and (10) to be equal. With the above potential this becomes, for $-T<t<T$,

$$\int_{-T}^{t}\int_{-\beta}^{\beta}\exp[i(t-u)(y-e_0)]a_0(u)dy\,du=\pi\mu a_0(t)\ . \tag{43}$$

Taking $\mu=\mu_R+i\mu_I$ and using (11), we can write a_0 in phase-factor form as

$$a_0(t)=\exp-\gamma_R(t+T)\exp-i\gamma_I(t+T)\ , \tag{44}$$

where $\gamma=\pi\mu V_0^2T^{-2}\beta^{-1}/4$. Substituting into (43), the phase factor can be considered as a perturbation to e_0 and, after making a change of variable $x=y-e_0+\gamma_I$, with appropriate change of limits to β_1 and β_2, the consistency condition becomes

$$\int_{-T}^{t}\int_{\beta_1}^{\beta_2}\exp[i(t-u)(x-i\gamma_R)]dx\,du=\pi\mu\ . \tag{45}$$

As explained earlier, the significant part of μ is the real part. Concentrating on this and integrating over u, we obtain

$$\mathrm{Re}[I_1+I_2\exp\gamma_R(t+T)]=\pi\mu_R \tag{46}$$

where

$$I_1=-\int_{\beta_1}^{\beta_2}\frac{1}{(\gamma_R+ix)}dx=\tan^{-1}\frac{\beta_1}{\gamma_R}-\tan^{-1}\frac{\beta_2}{\gamma_R}+\frac{i}{2}\ln\frac{\gamma_R^2+\beta_2^2}{\gamma_R^2+\beta_1^2} \tag{47}$$

and

$$\mathrm{Re}I_2=\int_{\beta_1}^{\beta_2}\left\{\frac{\gamma_R\cos\{(t+T)x\}}{\gamma_R^2+x^2}+\frac{x\sin\{(t+T)x\}}{\gamma_R^2+x^2}\right\}dx\ . \tag{48}$$

Since $\gamma_R=\pi\mu_R V_0^2T^{-2}\beta^{-1}/4$ Eq. (46) is a very complicated implicit equation of μ_R. If the WBA is correct, the solution of this equation should give values of μ_R equal to 0, 1 or $\frac{1}{2}$ depending on the position of e_0. Equation (46) also depends on time t and the values of μ_R should be independent of t. We now examine how far these tests of consistency are satisfied. To evaluate I_2, we define

$$I(q)=\int_{\beta_1}^{\beta_2}\frac{\cos(qx)}{\gamma_R^2+x^2}dx \tag{49}$$

so that

$$\mathrm{Re}I_2=-p(t+T)+\gamma_R I(t+T)\ , \tag{50}$$

where

$$\frac{dI}{dq}=p \tag{51}$$

and

$$\frac{dp}{dq}=\gamma_R^2 I-\frac{1}{q}\{\sin(q\beta_2)-\sin(q\beta_1)\}\ . \tag{52}$$

These can be solved using a standard Runge-Kutta method where $p(0)=0$ and

$$I(0)=\frac{1}{\gamma_R}\left\{\tan^{-1}\frac{\beta_2}{\gamma_R}-\tan^{-1}\frac{\beta_1}{\gamma_R}\right\}\ . \tag{53}$$

The effects of changing the bandwidths, the position of e_0, and the velocity can be considered by varying β_1 and β_2 and other parameters. It turns out to be most convenient to vary β_1, β_2, and the parameter m defined by

$$\ln(m)=-(T+t)\pi\mu_R V_0^2T^{-2}\beta^{-1}/4\ . \tag{54}$$

In Table I, we test the effect of varying β_1 and β_2 for various m. For $t=T$

$$m=|a_0(t)| \tag{55}$$

so that we can regard the results as testing the WBA for various values of $|a_0(T)|$ and fixed T. We recall that $e_0\approx 0$ and that $\beta_1-\beta_2=2\beta$ so that we can see that when e_0 is at the center of the band, for sufficiently large β, we obtain $\mu_R=1$. For a displaced position when $\beta_1=-1250$ and $\beta_2=3750$ again $\mu_R\approx 1$ and only at the band edge ($\beta_1=0,\beta_2=5000$) do we obtain $\mu_R\approx\frac{1}{2}$. For e_0 outside the band it is only valid to consider small changes in $a_0(t)$ so that we have only used $m=0.9$. We can see that near the band edge $\mu_R\approx 0.5$ but as the value of e_0 moves further away from the band $\mu_R\approx 0$.

Since the interaction potential has the simple form of (42) the results in Table I can be interpreted in an alternative way, namely that we are testing the WBA. From (54), we can interpret a change in the value of m from 1 to 0 as due to varying t from $-T$ to T while keeping the other parameters fixed. For Eq. (46) to be satisfied the left-hand side should show no variation with t, this is equivalent to the right-hand side of (56) showing no variation with m for fixed values of β_1 and β_2. This is borne out extremely well for most of the cases considered in the table. One exception is $\beta_2-\beta_1=400$ so the bandwidth is smaller than the other cases considered but even in this case the variation is quite small. However, for e_0 out of the band we cannot use $\mu_R\approx 1$. We conclude that, while this underlines the danger of using WBA in such situations, where e_0 is out of or near the band edge, in the more usual situations the numerical calculations completely confirm the theory developed.

In Table II we examine the effect of large velocities for the special case discussed in Sec. IV. To do this we choose $m=0.9$, $\beta_2=-\beta_1=2500$, and increase $-\ln(m)/T$, which corresponds to a decrease in T thus giving a model for increasing velocities. We see that μ_R decreases with decreasing T (that is increasing velocity) corresponding to smaller values of q in (41). Again we conclude that the numerical calculation confirms the theoretical prediction that it is not only the bandwidth but also the initial speed that is important in WBA.

VI. NONSYMMETRIC SDOS AS COMPOSITE UNIFORM BANDS

So far we have considered only SDOS which are symmetric about the band center. Nonsymmetric SDOS can be treated as sums of symmetrical SDOS (such as those considered in Sec. IV), but with each of the constituent symmetrical bands having a different band center. The arguments used earlier to show that the WBA can be assessed using uniform bands only will hold in the more

TABLE I. The variation of μ_R with m for different bands characterized by β_1 and β_2.

β_1	β_2	$m=0.9$	$m=0.7$	$m=0.5$	$m=0.3$	$m=0.1$
−200	200	1.02	1.01	0.99	0.94	1.00
−2000	2000	1.00	1.00	1.00	1.00	0.99
−5000	5000	1.00	1.00	1.00	1.00	1.00
0	5000	0.50	0.50	0.50	0.50	0.50
−1250	3750	1.00	1.00	1.00	1.00	1.00
0.5	5000.5	0.48	*	*	*	*
10	5010	0.17	*	*	*	*
50	5050	0.02	*	*	*	*

TABLE II. The variation of μ_R for fixed m and decreasing T, corresponding to increasing speed of the ion.

$-\ln(m)/T$	μ_R
1	1.00
10	0.99
500	0.35
1000	0.18
2000	0.09
5000	0.04
10 000	0.02

general case so it is enough to consider a composition of uniform bands.

Let

$$\rho_i(y;\beta_i,y_i)=\begin{cases}(2\beta_i)^{-1}, & |y-y_i|<\beta_i \\ 0 \quad \text{otherwise}\end{cases} \tag{56}$$

be the SDOS for a uniform band of width $2\beta_i$ with band center at $y=y_i$. We represent a composite uniform band by the SDOS

$$\rho(y)=\sum_{i=1}^{n} c_i\rho_i(y;\beta_i,y_i)\ , \tag{57}$$

where the c_i are positive constants. An example for $n=2$ is shown in Fig. 2.

Equation (7) will hold for the composite band provided we change the limits of integration for y to include the whole of the band. The new form for (9) is

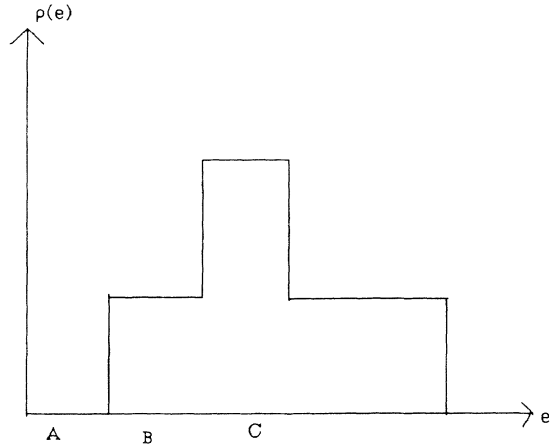

FIG. 2. SDOS for a composite of two uniform wide bands. With the orbital energy e_0 at A it is outside both wide bands; e_0 at B is within one band and outside the other; e_0 at C is within both bands.

$$\int_{\text{band}}\rho(y)\exp i(t-u)y\,dy=\sum_{i=1}^{n} c_i\exp i(t-u)y_i\int_{\beta_1}^{\beta_2}\rho_i(x;\beta_i,0)\exp i(t-u)x\,dx \tag{58}$$

so that (27) is replaced by

$$\frac{da_0}{dt}=-2V(t)\int_{-\infty}^{0} a_0(t+s)V(t+s)\pi\sum_{i=1}^{n} c_i\beta_i^{-1}f(\beta_i,s)\exp i(e_0+y_i)s\,ds\ . \tag{59}$$

In this equation the energy origin is arbitrary and the parameters y_i take into account the differing band centers of each component of the composite band.

If every component band is wide, then we can replace each $f(\beta_i,s)$ by $\delta^+(s)$ so that

$$\frac{da_0}{dt}=-V^2(t)\pi\left\{\sum_{i=1}^{n} c_i\beta_i^{-1}\mu_i\right\}a_0(t)\ . \tag{60}$$

The constants μ_i in (61) have the same properties as μ in Sec. IV. Thus, μ_i is 1, $\frac{1}{2}$, or 0 depending on whether e_0 is within, on an edge of, or outside the ith band. This is illustrated in Fig. 2 where A, B, and C are possible positions for e_0. In this two component example the transition probability is given by

$$P=1-\exp-\pi\left\{\frac{c_1\mu_1}{\beta_1}+\frac{c_2\mu_2}{\beta_2}\right\}\int_{-\infty}^{\infty} V^2(t)dt\ . \tag{61}$$

If e_0 is at position A we have $\mu_1=\mu_2\approx 0$ so that $P\approx 0$. If, however, e_0 is at B we have $\mu_1\approx 1$ and $\mu_2\approx 0$, whereas $\mu_1\approx\mu_2\approx 1$ at C. In practice the simple analysis given here will be complicated by the fact that e_0 depends on t so that it is not at any fixed position. Returning to the general expression (60) we find that, on integration, we obtain the standard WBA results of (11) and (12) but with $\mu\beta^{-1}$ replaced by $\sum_{i=1}^{n} c_i\beta_i^{-1}\mu_i$. Thus the WBA still holds for a composite uniform band provided each component is itself a wide band. We regard this as an important result since it shows that the WBA may be used for nonuniform and, considering Fig. 2, nonsymmetric surface densities of states.

VII. A MIXED WIDE AND NARROW BAND

It is possible to analyze also the case where there are several bands, some narrow and some wide. The method can be illustrated by considering the simplest example of two bands, one wide and one narrow. Two typical situations are illustrated in Figs. 3 and 4. Figure 3 is an idealization of the band structure for the wide s-p band in

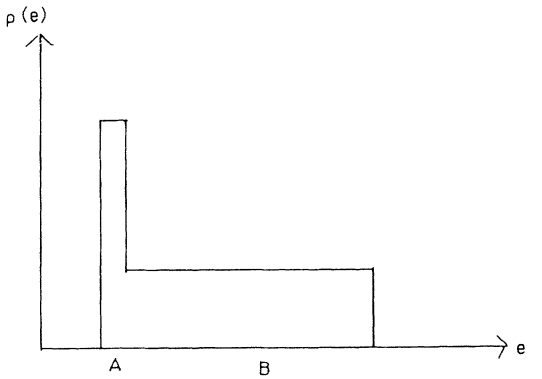

FIG. 3. SDOS for a composite of a uniform wide band with a uniform narrow band at a band edge. At A, e_0 is within the narrow band and at the edge of the wide band; e_0 at B is outside the narrow band and near the center of the wide band.

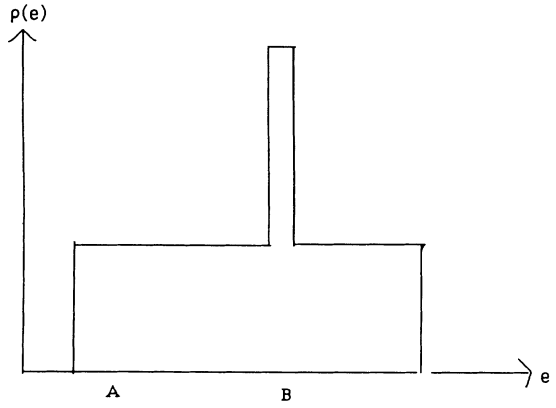

FIG. 4. Similar to Fig. 3 but with the narrow band near the center of the wide band. At A, e_0 is outside the narrow band but well within the wide band; at b, e_0 is within both.

copper. A similar structure is found in the transition metals but for these the d band is not completely full so that our RCT equations (1) and (2) would need to be augmented to properly account for that.

We will assume that the narrow band can be represented by a single band orbital ϕ_n, while the remaining band orbitals in (1) are associated with the wide band. Applying the WBA to those orbitals, (3) can be replaced by the following pair of equations:

$$\frac{da_0}{dt}=-\pi\mu_1 c_1\frac{V^2(t)}{\beta}a_0-i\sqrt{2}V(t)v_n b_n \ , \tag{62}$$

$$\frac{db_n}{dt}=-i(e_0-e_n)b_n-i\sqrt{2}v_n V(t)a_0 \ , \tag{63}$$

where b_n is the coefficient of the configuration describing the transfer of an electron from the narrow band to the ion and $c_2=v_n^2$. Writing $a_0(t)=A_0(t)\exp\chi(t)$ where

$$\chi(t)=\frac{-\pi c_1\mu_1}{\beta_1}\int_{-\infty}^{t}V^2(u)du \ , \tag{64}$$

Eqs. (62) and (63) become

$$\begin{aligned}\frac{dA_0}{dt}&=-i\sqrt{2}V(t)\exp\{-\chi(t)\}v_n b_n \ ,\\ \frac{db_n}{dt}&=-i(e_0-e_n)b_n-i\sqrt{2}v_n V(t)\exp\{\chi(t)\}A_0 \ .\end{aligned} \tag{65}$$

Equations (65) form a pseudo-two-level system and can easily be solved numerically for A_0 and b_n and hence $a_0(t)$. In extreme situations the solution is simpler, however. For example, with extremely large interactions where $V^2(t)\gg\beta_1$, we have $|a_0(t)|^2\approx 0$ and $P\approx 1$, so that ion neutralization is very likely. Similarly, if $\beta_1\gg V^2(t)$ the solution is closely approximated by the standard two-level problem since $\chi(t)\approx 0$ and so $\exp\{\chi(t)\}\approx 1$; consequently we would expect oscillations in the neutralization probability as a function of the initial speed, typical of narrow band situations.

If we now consider the situation described by Fig. 3 where the narrow band occurs at the edge of a wide band then $\mu_1\approx\frac{1}{2}$ at A and $\mu_1\approx 1$ at B. Since in the pure narrow band case significant transitions only occur at or near resonance we would expect that at B the major effect is from the wide band, whereas at A we would have an effect from the narrow band and, since $\mu_1\approx\frac{1}{2}$, a reduced effect from the wide band. For Fig. 4, the conclusions are similar with the wide band dominating at position A and a cumulative effect at position B. For this case, however, at position B, the effect of the wide band is not reduced since $\mu_1\approx 1$.

An important example of this would arise where there is a narrow band of surface states at the edge of a wide band (similar to Fig. 3). A particular case of this arises with Li^+ scattered off Si(100), whereas full numerical treatment of the MET equations produces results characteristic of a narrow band since the Li^+ energy is aligned with surfaces states at closest approach.[9] This is in line with the theory of the previous paragraph.

This analysis shows that it is possible to combine the two standard approximations, the narrow band and the wide band approximations, for a more general situation. In the case considered we have derived a new two-level problem for the case of a narrow band represented by one state and a wide band. Clearly the narrow band analysis can be generalized to include more states, or to several narrow bands, giving rise to a n-level problem for more complex cases.

ACKNOWLEDGMENTS

The authors are grateful for many enlightening discussions with Dr. K. W. Sulston, Professor S. G. Davison, and Dr. Z. Miskovic.

APPENDIX A

In the cases where the ion does not get close to the surface, it is a reasonable approximation to regard e_0 as a constant. In general we can choose an origin for the coordinates in the substrate (usually at the target atom) so that the $\{e_k\}$ are independent of time, but in the situations where the ion gets close to the surface, u_0 and e_0 depend on time. In this Appendix we examine how the analysis is affected by this time dependence.

It can be shown that the equations are essentially unchanged when u_0 and e_0 depend on time,[8] so that we can treat this time dependence by reconsidering (3) with e_0 depending on t. This dependence can be expressed by the equation

$$e_0=e_0[z(t)] \ , \tag{A1}$$

where z is the distance of the ion from the origin in the substrate. Thus

$$\frac{de_0}{dt}=\frac{de_0 dz}{dzdt} \tag{A2}$$

and for slow ions dz/dt is small. Furthermore we may assume that de_0/dz is not large so that $e_0'(t)$ is small. The time dependence of e_0 may be allowed for in (27) by replacing $f(\beta,s)\exp(ie_0 s)$ with

$$f(\beta,s)\exp\left[-i\int_{t+s}^{t}e_0(x)\right]dx \ . \tag{A3}$$

As discussed in Sec. IV, $f(\beta,s)\approx 0$ unless $|s|<n\beta^{-1}$ for some relatively small n, so that we only need to consider (A3) for $n\beta^{-1}\le s\le 0$. In this interval we may use Taylor's theorem for $e_0(x)$ so that

$$\int_{t+s}^{t}e_0(x)dx=\int_{t+s}^{t}[e_0(t)+(x-t)e_0'(\bar{\chi})]dx \ , \tag{A4}$$

where $\bar{\chi}$ is between x and t. Thus

$$\int_{t+s}^{t}e_0(x)dx=-e_0(t)s+\eta \tag{A5}$$

where

$$|\eta|<(\max|e_0'(x)|)\frac{n^2}{\beta^2} \ . \tag{A6}$$

Since $e_0'(x)$ is small and we have a wide band then η will be small so that (A3) can be approximated by

$$f(\beta,s)\exp[ie_0(t)s]=f(\beta,s)\exp[ik(t)\beta s] \ . \tag{A7}$$

Thus the analysis developed in Sec. IV may be applied, but k depends on t, and hence μ depends on t. If, throughout the interaction, $e_0(t)$ is in resonance with the band so that

$$-1<k(t)<1 \tag{A8}$$

then $\mu=1$ and the analysis is unchanged. In more general situations μ will vary, but for monotonic $e_0(t)$ during both the inward and outward trajectories there are two typical cases. The first of these is where e_0 is initially out of the band, comes into resonance at $t=-T_1$, and goes out of resonance at $t=T_2$. ($T_1,T_2>0$ and for a symmetric trajectory $T_1=T_2$.) For this situation we may take $\mu=1$, $-T_1<t<T_2$, and 0 otherwise. This assumes that we can ignore the effect of the transition periods at $t\approx -T_1$ and $t\approx T_2$, when e_0 is near the band edges. The second case is when e_0 is initially in resonance, goes out of resonance at $t=-T_1$, and into resonance again at $t=T_2(T_1,T_2>0)$. A similar analysis leads to $\mu=0$, $-T_1<t<T_2$, and 1 otherwise.

Thus, provided e_0 can be determined throughout the trajectory, the applicability of the WBA is not affected by allowing u_0 and e_0 to depend on t.

APPENDIX B

Here we briefly examine how our analysis is affected by more sophisticated models of RCT. These models include configurations which describe the transfer of an electron from the band into an initially unoccupied band orbital via the atom. For these more general models Eq. (3) has the form

$$i\frac{da_0}{dt}=\sqrt{2}V(t)\sum_{k=1}^{n}v_k b_k \ , \tag{B1}$$

$$i\frac{db_k}{dt}=(e_0-e_k)b_k+\sqrt{2}V(t)a_0+\sum_{jp}q_{kp}c_{kjp}v_j V(t) \ , \tag{B2}$$

$$i\frac{dc_{kjp}}{dt}=(e_j-e_0)c_{kjp}+q_{kp}v_j V(t)b_k \ . \tag{B3}$$

$k=1,\ldots,n$, $j=n+1,\ldots,m+n$, and p is an index for the degenerate spin-state configurations whose coefficients are c_{kjp}. Here $\{e_j\}$ denote the orbital energies of the unoccupied band orbitals and the values of q_{kp} depend on the particular basis of the spin-state configurations chosen.[8,9] The equations are to be solved subject to $a_0(-\infty)=1, b_k(-\infty)=c_{kjp}(-\infty)=0$. This model would be applicable in the case where the band is not full, as for a conductor, or for a semiconductor with a narrow gap between two separate bands, one of which is occupied. Integrating (B3) and substituting into (B2), with $\Delta_k=e_0-e_k$ and $\Delta_j=e_j-e_0$, we obtain

$$i\frac{db_k}{dt}=\Delta_k b_k+\sqrt{2}v_k V(t)a_0-iV(t)\sum_{jp}q_{kp}^2v_j^2\int_{-\infty}^{t}\exp[i\Delta_j(u-t)]V(u)b_k(u)du \ . \tag{B4}$$

Assuming both bands (or subbands) are wide and that the speed of the ion is slow, we can use WBA twice to obtain an expression for $a_0(t)$. Using the WBA for the last term in (B4) leads to

$$i\frac{db_k}{dt}=\Delta_k b_k+\sqrt{2}v_k V(t)a_0-iV^2(t)\mu_{1k}\frac{\pi}{\beta}b_k \tag{B5}$$

so that

$$b_k=-i\sqrt{2}v_k\int_{-\infty}^{t}\exp[i\Delta_k(u-t)]\exp\left[\int_t^u\mu_{1k}\frac{\pi}{\beta}V^2(x)dx\right]V(u)a_0(u)du \ . \tag{B6}$$

Substituting into (B1) gives

$$\frac{da_0}{dt}=-2V(t)\sum_{k=1}^{n}v_k^2\int_{-\infty}^{t}\exp(i\Delta_k(u-t)\exp\left[\int_t^u\mu_{1k}\frac{\pi}{\beta}V^2(x)dx\right]V(u)a_0(u)du \ . \tag{B7}$$

Note that the values of μ_{1k} incorporate the factor of $\frac{1}{2}$ discussed earlier, the sums of q_{kp}^2 over p, and the sum of v_j^2 over j. In the case where e_0 is not in resonance with the unoccupied band (or subband) we have $\mu_{1k}=0$ for all k. Applying the WBA we may write (A7) as

$$\frac{da_0}{dt}=-\mu_2 V^2(t)\frac{\pi}{\beta}a_0(t) \tag{B8}$$

which is of the same form as (10). Thus the more sophisticated model leads to the same expression for $a_0(t)$ with $\mu_2=0$, $\frac{1}{2}$, or 1 depending on the position of e_0 relative to the occupied band (or subband). However, the neutralization probability is now given by

$$|a_0(t)|^2+\sum_{kjp}|c_{kjp}(t)|^2 . \tag{B9}$$

We note that for the separate bands (subbands) considered, for any particular time, e_0 cannot be in resonance with both bands. In particular if, throughout the interaction, e_0 is in resonance with the occupied band (subband), then we have $c_{kjp}=0$ for all t and the original model is sufficient to describe the interaction.

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