A time-dependent embedding calculation of surface electron emission

J E Inglesfield

School of Physics and Astronomy, Cardiff University, The Parade, Cardiff, CF24 3AA, UK

E-mail: JE.Inglesfield@googlemail.com

Received 2 May 2011, in final form 10 June 2011
Published 1 July 2011
Online at stacks.iop.org/JPhysCM/23/305004

Abstract

The Dirac–Frenkel variational principle is used to derive the embedding method for solving the time-dependent Schrödinger equation. Embedding allows the time evolution of the wavefunction to be calculated explicitly in a limited region of space, the region of physical interest, the embedding potential ensuring that the wavefunction satisfies the correct boundary conditions for matching on to the rest of the system. This is applied to a study of the excitation of electrons at a metal surface, represented by a one-dimensional model potential for Cu(111). Time-dependent embedding potentials are derived for replacing the bulk substrate, and the image potential and vacuum region outside the surface, so that the calculation of electron excitation by a surface perturbation can be restricted to the surface itself. The excitation of the Shockley surface state and a continuum bulk state is studied, and the time structure of the resulting currents analysed. There is a distinction between emission from the localized surface state, where the charge is steadily depleted, and the extended continuum state, where the current emitted into the vacuum is compensated by current approaching the surface from the bulk. The time taken for the current to arrive outside the surface is studied.

1. Introduction

The question ‘How long does it take?’ arises in many areas of condensed matter physics, in photoemission from surfaces [1], electron tunnelling through barriers [2, 3], relaxation after the creation of a core hole [4] and so on. In this paper we shall study the time-dependence of electron emission from a metal surface, using an embedding formalism which we have recently developed [5] and now further improved.

The development of attosecond streaking spectroscopy, using ultra-short laser pulses, has raised interesting questions about the time it takes for electrons to be emitted in photoemission [1], and recent computational studies have tackled this problem [6, 7]. In these time-dependent calculations, the surface and substrate are represented by a slab with a finite region of vacuum outside, and sooner or later an electron excited by the time-dependent perturbation reaches the boundary of the calculation. How to deal with this is a familiar problem in time-dependent calculations in atomic physics, and it is often handled (as in the calculations just mentioned) by introducing an absorbing potential at the boundary [8]. It is important to eliminate spurious back reflections, and exact boundary potentials have been developed which ensure that the wavefunction has the correct boundary conditions to match on to the rest of space [9, 10]. This is also the idea of embedding [5, 11]: we solve the Schrödinger equation in the region of space of interest, which we call region I, with an embedding potential at the boundary of the region to ensure that the wavefunction matches correctly on to the external region, region II.

The original time-independent embedding method [11] has proved useful for calculations of surface electronic structure [12]—only the surface region, the top few atomic layers plus the near-surface vacuum region are treated explicitly, the bulk crystal and the semi-infinite vacuum being replaced by embedding potentials derived from the substrate Green functions. The embedding method treats the bulk continuum states at the surface, as well as localized surface states correctly, and gives a very accurate description of surface electronic structure [13]. Our time-dependent embedding method builds on time-independent embedding and in the previous paper [5] we transformed the embedding potential as a function of energy into a function of time, and developed an embedded time-dependent Schrödinger equation for region I.

This time-dependent embedding used the results of earlier papers in which the problem of the exact termination of the spatially discretized Schrödinger equation was studied [10, 14]. However, in our method, we use a basis...
The idea of embedding is that we solve the Schrödinger equation explicitly in the region of interest, region I, the rest of the system, region II, being replaced by an embedding potential over the interface S between the regions. As in earlier surface embedding work [23], in the applications in this paper we take region I to be the surface region, that is, the top few atomic layers plus the adjacent image potential + vacuum region, and region II to be the rest of the system, the semi-infinite crystal substrate on one side, and the semi-infinite vacuum on the other.

The central quantity in embedding theory is the embedding potential, which relates the normal derivative and amplitude of \( \psi \), the solution of the Schrödinger equation in region II, over interface S. In the time-independent case [11] we have

\[
\frac{\partial \psi(r_S)}{\partial n_S} = -2 \int_S d\vec{r}_S' G_0^{-1}(r_S, r'_S; \epsilon) \psi(r'_S),
\]

where \( G_0^{-1}(r_S, r'_S; \epsilon) \) is the embedding potential evaluated at energy \( \epsilon \), the energy at which \( \psi \) is evaluated. The notation reflects the fact that \( G_0^{-1}(r_S, r'_S; \epsilon) \) is an inverse over S of the Green function in region II with zero normal derivative on S. The normal derivative on the left-hand side of (1) is evaluated outwards from region I into II. In time-dependent embedding, the analogous relationship for the solution of the time-dependent Schrödinger equation is given by [10, 14]

\[
\frac{\partial \psi(r_S, t)}{\partial n_S} = -2 \int_S d\vec{r}_S' \int_{-\infty}^{t} dt' \tilde{G}_0^{-1}(r_S, r'_S; t-t') \frac{\partial \tilde{\psi}(r'_S, t')}{\partial t'},
\]

with the embedding potential

\[
\tilde{G}_0^{-1}(r_S, r'_S; t) = \frac{1}{2\pi} \int_{-\infty}^{t} \epsilon d\epsilon \exp(-i\epsilon(t-t')) G_0^{-1}(r_S, r'_S; \epsilon).
\]

Equation (2) is almost the Fourier transform of (1), but it contains the time-derivative \( \partial \tilde{\psi}/\partial t' \); this compensates for the convergence factor of \(-1/\epsilon\) in the transform (3) of the embedding potential. When we evaluate this transform, we take \( \epsilon \) to lie just above the real axis, above the singularities in the Green function, so that \( \tilde{G}_0^{-1}(t) = 0 \) for \( t < 0 \).

We wish to study the time evolution of bulk continuum states at the surface, as well as the discrete surface states, under the influence of a time-dependent perturbation confined to region I. However, the initial wavefunction extends beyond region I—obviously so for continuum states, but even the exponentially decaying surface states extend some distance into the bulk and vacuum into region II. The time evolution of such states was treated in the previous paper [5], but here we use the Dirac–Frenkel variational principle [17, 18] to develop the formalism more consistently. This states that the solution \( \Psi(r, t) \) of the time-dependent Schrödinger equation over the whole of space satisfies

\[
\delta I = \int_{I+II} d\vec{r} \delta \Psi^* \left[ H - i \frac{\partial}{\partial t} \right] \Psi(r, t) = 0,
\]

for small variations \( \delta \Psi^* \).

The unperturbed wavefunction \( \Sigma(r, t) \) is a stationary state of the Hamiltonian \( H_0 \),

\[
H_0 = -\frac{1}{2} \nabla^2 + V(r),
\]
where \( V(\mathbf{r}) \) is the time-independent potential in \( I + II \), and
\[
\Xi(\mathbf{r}, t) = \xi(\mathbf{r}) \exp(-iEt), \quad \text{with } H_0\xi = E\xi. \tag{6}
\]
We now switch on the perturbing potential \( \delta V(\mathbf{r}, t) \) in region \( I \) at time \( t = 0 \), and see how this wavefunction develops. Writing the full time-dependent Hamiltonian as \( H \) and the evolving wavefunction as \( \Psi \) we have
\[
H = H_0, \quad \Psi(\mathbf{r}, t) = \Xi(\mathbf{r}, t), \quad t \leq 0, \tag{7}
\]
and for \( t > 0 \),
\[
H = H_0 + \delta V(\mathbf{r}, t), \quad \Psi(\mathbf{r}, t) = \Xi(\mathbf{r}, t) + \phi(\mathbf{r}, t), \tag{8}
\]
\( \mathbf{r} \) in region \( I \)
\[
H = H_0, \quad \Psi(\mathbf{r}, t) = \Xi(\mathbf{r}, t) + \psi(\mathbf{r}, t), \tag{9}
\]
\( \mathbf{r} \) in region \( II \).

Here, \( \phi(\mathbf{r}, t) \) is a trial function in region \( I \), and \( \psi(\mathbf{r}, t) \) is the exact solution of the time-dependent Schrödinger equation in region \( II \), which matches in amplitude on to \( \phi(\mathbf{r}_s, t) \) over \( S \) as \( \phi \) may not be the exact solution of the Schrödinger equation, they do not necessarily match in derivative. \( \Xi \) + \( \psi \) satisfies the time-dependent Schrödinger equation in region \( II \), and the functional variation (4) reduces to a volume integral in region \( I \) and a surface contribution over \( S \) coming from the kinetic energy operator \(-\frac{1}{2}\nabla^2 \) acting on the discontinuity in derivative,
\[
\delta I = \int_I d\mathbf{r} \phi(\mathbf{r}, t) \left[ H\phi(\mathbf{r}, t) + \delta V \Xi(\mathbf{r}, t) - i\frac{\partial \phi(\mathbf{r}, t)}{\partial t} \right] + \frac{1}{2} \int_S d\mathbf{s} \delta \phi(\mathbf{r}_s, t) \left[ \frac{\partial \phi(\mathbf{r}_s, t)}{\partial n_s} - \frac{\partial \psi(\mathbf{r}_s, t)}{\partial n_s} \right], \tag{10}
\]
now with a lower limit of the time integral of \( t = 0 \), and the variation of the functional simplifies to
\[
\delta I = \int_I d\mathbf{r} \phi(\mathbf{r}, t) \left[ H\phi(\mathbf{r}, t) + \delta V \Xi(\mathbf{r}, t) - i\frac{\partial \phi(\mathbf{r}, t)}{\partial t} \right] + \frac{1}{2} \int_S d\mathbf{s} \delta \phi(\mathbf{r}_s, t) \frac{\partial \phi(\mathbf{r}_s, t)}{\partial n_s} \left[ \frac{\partial \phi(\mathbf{r}_s, t)}{\partial n_s} - \frac{\partial \psi(\mathbf{r}_s, t)}{\partial n_s} \right] \times \tilde{G}_0^{-1}(\mathbf{r}_s, \mathbf{r}_s'; t - t'), \tag{11}
\]
This expression only involves region \( I \) and its boundary surface \( S \), the final embedding term accounting for the rest of the system.

To find \( \phi(\mathbf{r}, t) \) such that \( \delta I = 0 \) for all variations, we use a basis set expansion,
\[
\phi(\mathbf{r}, t) = \sum_m a_m(t) \chi_m(\mathbf{r}) \tag{12}
\]
— it is convenient both in the formalism and in coding if the basis functions \( \chi_m \) are orthonormal when integrated over region \( I \)—and substituting into (11) gives
\[
\delta I = \sum_{mn} \delta a_m(t) \tilde{H}_{mn}(t) a_n(t) + \sum_{mn} \delta a_m(t) e_n(t) \frac{\partial a_n(t)}{\partial t} \tag{13}
\]
\( \tilde{H}_{mn}(t) \) is the embedding matrix which includes the surface derivative term in (11) as well as the perturbing potential,
\[
\tilde{H}_{mn}(t) = \frac{1}{2} \int_I d\mathbf{r} \nabla \chi_m(\mathbf{r}) \cdot \nabla \chi_n(\mathbf{r}), \tag{14}
\]
the embedding matrix \( \tilde{\Sigma}_{mn} \) is given by
\[
\tilde{\Sigma}_{mn}(t) = \int_S d\mathbf{s} \int_S d\mathbf{s}' \chi_m(\mathbf{r}_s) \tilde{G}_0^{-1}(\mathbf{r}_s, \mathbf{r}_s'; t) \chi_n(\mathbf{r}_s), \tag{15}
\]
and vector \( e_n(t) \) comes from the unperturbed state,
\[
e_n(t) = \int_I d\mathbf{r} \chi_m(\mathbf{r}) \delta V(\mathbf{r}, t) \Xi(\mathbf{r}, t). \tag{16}
\]

The variational principle \( \delta I = 0 \) for all variations \( \delta a_m(t) \) then implies
\[
\sum_n \left[ \tilde{H}_{mn}(t)a_n(t) + \int_0^t dt' \tilde{\Sigma}_{mn}(t - t') \frac{\partial a_n(t)}{\partial t} \right] + e_n(t) = \frac{\partial a_m(t)}{\partial t}, \quad t > 0, \tag{17}
\]
an inhomogeneous time-dependent matrix equation which we can solve for \( a_m(t) \) with the initial condition that \( a_m(t = 0) = 0 \). Knowing the expansion coefficients \( a_m(t) \) gives us \( \phi \), hence \( \Psi \)—the time-evolving wavefunction in region \( I \), embedded on to the rest of the system.

3. Surface embedding potentials

In the previous paper [5] we applied time-dependent embedding to study excitations at a jellium surface, but here we shall consider a more realistic model of the surface, one which can support surface states as well as the bulk continuum. This is the one-dimensional model potential \( V(z) \) developed by Chulkov et al [19, 20], which has the form
\[
V(z) = \begin{cases} 
A_1 \cos(2\pi z/\lambda), & z < 0 \\
-A_{10} - A_{20} + A_2 \cos(\beta z), & 0 < z < z_1 \\
-A_{10} + A_3 \exp[-\alpha(z - z_1)], & z_1 < z < z_{im} \\
-A_{10} + \exp[-\lambda(z - z_{im})] & -1/4(z - z_{im}), \quad z > z_{im}.
\end{cases} \tag{18}
\]
Here \( \alpha \) is the interlayer spacing, parameter \( A_1 \) reproduces the width of the bulk energy gap, \( A_{10} \) is the inner potential, and \( A_2 \) and \( \beta \) are fitted to surface state energies. The remaining
parameters, including \( z_{\text{im}} \), the position of the image plane, are found by the requirement that the potential and its derivative are continuous across all the boundaries. Figure 1 shows the resulting surface potential for Cu(111) calculated with the parameters given in table 1; the zero of energy is taken as the average bulk potential.

To calculate the time-dependent embedding potentials from (3), we need the energy-dependent embedding potentials, \( G_v^{-1}(\epsilon) \) for embedding the surface region on to the semi-infinite crystal substrate at \( z_c \), and \( G_v^{-1}(\epsilon) \) for embedding on to the vacuum Coulomb tail. The Schrödinger equation is integrated between \( z_o \) and \( z_c \) to find \( G_v^{-1}(\epsilon) \).

As we have shown elsewhere [24], the first step in finding \( G_v^{-1}(\epsilon) \) is to integrate the Schrödinger equation at energy \( \epsilon \) through a bulk unit cell in each direction to give two independent solutions, \( \phi_1 \) and \( \phi_2 \). Taking the unit cell to lie between \( z_o \) and \( z_c \) (figure 1), the boundary conditions for determining \( \phi_1 \) and \( \phi_2 \) are as follows,

\[
\begin{align*}
\phi_1(z_o) &= 1, & \phi_1'(z_d) &= 0, & \text{integrate from } z_o \text{ to } z_c \\
\phi_2(z_o) &= 1, & \phi_2'(z_d) &= 0, & \text{integrate from } z_c \text{ to } z_o.
\end{align*}
\]

The corresponding wavevector \( k \) of the bulk band structure is then given by the remarkably simple expression

\[
\cos(ka) = \frac{\phi_1(z_c) + \phi_2(z_o)}{2}.
\]

—a related result has been given by Butti [25], and earlier by Kohn [26]. Using the property that it is a logarithmic derivative, it can be shown [24] that the embedding potential for embedding on to the semi-infinite crystal to the left of \( z_c \) is given by

\[
G_v^{-1}(\epsilon) = \frac{W(\phi_1, \phi_2)}{2[\exp(-ik\lambda) - \phi_1(z_c)]},
\]

where \( W \) is the Wronskian. For causality, the Schrödinger equation is solved at \( \epsilon \) with a positive imaginary part (which may be infinitesimal), and \( k \) is chosen to have negative imaginary part, corresponding to a wave travelling or decaying into the crystal to the left.

In the vacuum region outside the crystal, the electron asymptotically feels the Coulomb tail of the image potential,

\[
V(z) = -A_1 - \frac{1}{4(z - z_{\text{im}})},
\]

in terms of the Chulkov potential parameters (18). We find the energy-dependent embedding potential from the logarithmic derivative expression (1), which in one dimension simplifies to

\[
G_v^{-1}(\epsilon) = -\frac{1}{2} \frac{\psi'(z_c)}{\psi(z_c)},
\]

where \( \psi(z) \) is the outgoing or decaying solution of the Schrödinger equation. This is a combination of the regular and irregular Coulomb functions \( F_0 \) and \( G_0 \) with angular momentum \( L = 0 \), in the notation of the NIST Handbook [27],

\[
\psi(z) = H_0^{-}(\eta, \rho) = G_0(\eta, \rho) - iF_0(\eta, \rho)
\]

with arguments given by

\[
\rho = \sqrt{2(\epsilon + A_1)}(z_{\text{im}} - z), \quad \eta = \frac{1}{4\sqrt{2(\epsilon + A_1)}}.
\]

Thompson and Barnett [28] give a rapidly converging continued fraction expression for \( H_0^{-}/H_0^{+} \), from which we immediately obtain \( G_v^{-1}(\epsilon) \) using (23).

We can use these embedding potentials to find the surface density of states for Cu(111), by evaluating the Green function of the embedded Schrödinger equation \( G(z, z'; \epsilon) \). The local density of states at energy \( E \) is then given by [11]

\[
\sigma(z, E) = \frac{1}{\pi} \text{Im} G(z, z; \epsilon),
\]

where \( \epsilon = E + i\eta \), and the small imaginary term \( \eta \) gives energy broadening. Integrating \( \sigma(z, E) \) over the surface region gives the surface density of states, the number density of electrons with energy \( E \). This is shown in figure 2, with region I taken between \( z_c = -10 \text{ au} \) and \( z_c = +10 \text{ au} \), and \( \eta = 1 \times 10^{-5} \text{ au} \)—full details of the calculation are given in an earlier preprint [24]. The results show the Shockley surface

### Table 1. Parameters used in the Chulkov potential for Cu(111) for different regions near the surface. \( a, A_1, A_{10}, A_2 \text{ and } \beta \) are tabulated by Chulkov et al [20], and the other parameters are derived; all parameters are given in atomic units.

| Region with \( z < 0 \) | \( a = 3.94 \) | \( A_1 = 0.1889 \) |
|--------------------------|-----------------|-----------------|
| \( 0 < z < z_1 \) | \( \beta = 2.9416 \) | \( A_{10} = -0.43713 \) |
| \( z_1 < z < z_{\text{im}} \) | \( \alpha = 0.63650, z_1 = 1.33499 \) | \( A_2 = 0.15905 \) |
| \( z > z_{\text{im}} \) | \( \lambda = 1.27330 \) | \( A_{20} = 0.40729 \) |

**Figure 1.** One-dimensional potential for modelling the Cu(111) surface [20]. At \( z_c \) the surface region is embedded on to the semi-infinite crystal potential, and at \( z_c \) it is embedded on to the vacuum Coulomb tail. The Schrödinger equation is integrated between \( z_o \) and \( z_c \) to find \( G_v^{-1}(\epsilon) \).
state at $E = 0.2415$ au, close to the bottom of the band gap at $0.2201$ au, with the first image state at $E = 0.4072$ au, immediately below the top of the gap at $0.4087$ au [29]; the higher members of the image series overlap the continuum and become resonances. For comparison, the Fermi energy is at 0.2556 au [20] and the vacuum zero at 0.4371 au (table 1). A caveat is that the Chulkov potential is designed to describe the band gap (figure 2).

Figure 2. Surface density of states of Cu(111), the local density of states integrated through region I, taken between $z_c = -10$ au and $z_c = +10$ au. Energy broadening is $1 \times 10^{-5}$ au.

In this section we show how to calculate the time evolution of wavefunctions at the metal surface using the embedding formalism and the embedding potentials developed in section 6, and test the accuracy of the method. We assume

$$G_{\text{c}}^{-1}(\epsilon) = \begin{cases} \frac{-\sqrt{\epsilon/2}}{1-i\sqrt{\epsilon/2}} & \epsilon < 0 \\ 0 & \epsilon > 0 \end{cases}$$

$$G_{\text{t}}^{-1}(t) = \begin{cases} 0 & t < 0 \\ \frac{1-i}{2\sqrt{\pi t}} & t > 0 \end{cases},$$

where the free-electron embedding potentials are given by [5, 10, 14]

$$G_{\text{c}}^{-1}(\epsilon) = \int_{-\infty}^{+\infty} \frac{\exp(-i\epsilon t)}{\epsilon} \times [G_{\text{c}}^{\text{f}}(\epsilon) - G_{\text{t}}^{-1}(\epsilon)] + G_{\text{t}}^{-1}(t),$$

and we can ensure rapid convergence of the integral by taking the Fourier transforms of $G_{\text{c}}^{\text{f}}(\epsilon)$ and $G_{\text{t}}^{-1}(\epsilon)$, respectively, with the extra factor of $\frac{1}{\epsilon}$ (3). At large $|\epsilon|$, the energy-dependent embedding potentials have free-electron behaviour, proportional to $|\epsilon|^{1/2}$, and we can use rapid convergence of the integral by subtracting this off and adding on the corresponding time-dependent potential,$$
\bar{G}_{\text{c}}^{-1}(t) = \frac{i}{2\pi} \int_{-\infty}^{+\infty} \frac{\exp(-i\epsilon t)}{\epsilon}$$

Figure 3 shows the time-dependent embedding potential for Cu(111) evaluated at $z_c = -10$ au. Curves a and b, real and imaginary parts of $[\bar{G}_{\text{c}}^{-1}(t) - \bar{G}_{\text{t}}^{-1}(t)]$; curves c and d, real and imaginary parts of $\bar{G}_{\text{t}}^{-1}(t)$.

Figure 3. Time-dependent embedding potential for Cu(111) evaluated at $z_c = -10$ au. Curves a and b, real and imaginary parts of $[\bar{G}_{\text{c}}^{-1}(t) - \bar{G}_{\text{t}}^{-1}(t)]$; curves c and d, real and imaginary parts of $\bar{G}_{\text{t}}^{-1}(t)$.
that the electrons are excited from their stationary states by a surface perturbation given by

$$
\delta V(z, t) = A \exp \left(-\left(z^2 / \Delta \right) \sin(\omega t) \right),
$$

-switched on at \( t = 0 \). To expand \( \phi(z, t) \) (12) in this one-dimensional calculation we use trigonometric basis functions,

$$
\chi_m(z) = \begin{cases} 
\cos \left(\frac{m \pi \xi}{2} \right), & m \text{ even}, \\
\sin \left(\frac{m \pi \xi}{2} \right), & m \text{ odd},
\end{cases}
$$

where \( \xi \) is measured from the mid-point of region I,

$$
\xi = z - \frac{z_c + z_v}{2}. \tag{31}
$$

Choosing a value of \( D \gg (z_c - z_v)/2 \) gives a range of logarithmic derivatives at \( z_c \) and \( z_v \) for matching on to the embedding potentials, and we subsequently orthogonalize the basis functions over region I. The unperturbed wavefunction \( \xi(z) \) (6) and (7), which enters the time-evolution equation through vector \( e \) (16), can be efficiently calculated using the Numerov method [30], integrating inwards from the vacuum. Energy normalization is used when \( \xi \) is a continuum state [22], so that the electron density equals the local density of states; when \( \xi \) is a discrete surface state, it is normalized to unity over all space.

To solve the time-dependent Schrödinger equation, we write equation (17) in abstract notation,

$$
\frac{da}{dt} = -i[H \psi + \Gamma]. \quad \text{where } \Gamma = e + \int_0^f dt' \bar{\Sigma}(t-t') \frac{da}{dt'}. \tag{32}
$$

To first order in the time interval \( \delta t \), and using central differences, we have

$$
a(t + \delta t) = a(t) - i\delta t \bar{H}(t + \delta t/2)a(t) - i\delta t \Gamma(t + \delta t/2). \tag{33}
$$

or alternatively,

$$
a(t + \delta t) = a(t) - i\delta t \bar{H}(t + \delta t/2)a(t) - i\delta t \Gamma(t + \delta t/2). \tag{34}
$$

Adding (33) and (34) gives

$$
a(t + \delta t) = \left[ 1 + \frac{i\delta t}{2} H(t + \delta t) \right]^{-1}
$$

$$
\times \left[ 1 - \frac{i\delta t}{2} H(t + \delta t) \right] a(t) - i\delta t \Gamma(t + \delta t/2) \right. \tag{35}
$$

the formula we use to advance the wavefunction expansion coefficients forward in time.

Although (35) turns out to be very accurate—much more so than the time-evolution method we described in [5]—it is only stable for small \( \delta t \). Because the trigonometric functions in (30) are defined with respect to \( 2D \), but used within the smaller embedding range, there is the risk of overcompleteness, and the closer we are to linear dependency in the basis set, the smaller the time interval \( \delta t \) needed for stability. Taking an embedding range \( (z_c - z_v) \) of 20 au, and \( 2D = 24 \) au, \( \delta t = 0.002 \) au gives stability up to 40 basis functions. With an embedding range of 40 au and \( 2D = 44 \) au this time interval gives stability up to 75 basis functions. Bringing \( 2D \) closer to the embedding range helps matters, and we find that with \((z_c - z_v) = 20 \) au, \( 2D = 22 \) au, and 30 basis functions we can go up to \( \delta t = 0.016 \) au without significant loss of accuracy. It is tempting to take \( 2D \gg (z_c - z_v) \) to eliminate the possibility of overcompleteness. However, for a given size of basis set this is less accurate, and it is much better to use a basis set with \( 2D > (z_c - z_v) \), giving a range of derivatives at the embedding surfaces.

To test the embedding method and the embedding potentials, we calculate the time evolution of the Shockley surface state at \( E = 0.2415 \) au (figure 2) with different embedding surfaces. In the time-dependent perturbation (29) we use a width parameter \( \Delta = 2 \) au and amplitude \( A = 0.2 \) au, with a frequency \( \omega = 0.5 \) au. First we consider a narrow surface region with \( z_c = -10 \) au, \( z_v = +10 \) au, using the basis set with \( 2D = 24 \) au and 40 basis functions, and a time interval of \( \delta t = 0.002 \) au. In the second case region I is wider, with \( z_c = -20 \) au, \( z_v = +20 \) au; we use a basis set with \( 2D = 44 \) au, 70 basis functions, and the same time interval of \( \delta t = 0.002 \) au. The results for the two calculations of the electron density evolved to \( t = 200 \) au are shown in figure 5. The difference between the two curves is barely visible, even in the magnified inset showing the results around \( z_c = -10 \) au.

Another interesting test is to look at the number of electrons in the embedded region, \( Q(t) \), as a function of time,

$$
Q(t) = \int_{z_c}^{z_v} dz |\psi(z, t)|^2. \tag{36}
$$

Continuity of charge requires

$$
Q(t) + J_c(t) + J_r(t) = \text{constant}, \tag{37}
$$

where \( J_c \) and \( J_r \) are the time-integrated currents leaving region I across the left- and right-hand embedding surfaces,

$$
J_{c/r}(t) = \int_0^t dt' j_{c/r}(t'), \quad j_{c/r}(t) = \mp \text{Im } \Psi^* \frac{\partial \Psi}{\partial z} \bigg|_{z_c/z_v}. \tag{38}
$$
We use the embedding formula (2) to calculate the normal derivative in this expression for the current. Taking region I between ±20 au, 70 basis functions with $2D = 44$ au, and using $\delta t = 0.002$ au, we calculate the time evolution of the surface state at 0.2415 au under the influence of the same surface perturbation as in the previous test. The results are shown in figure 6, and we see the steady decrease in the surface state charge in the surface region as time progresses. However, the continuity equation (37) is satisfied remarkably accurately, with $[Q(t) + J_0(t) + J_1(t)]$ staying almost perfectly constant—the maximum variation is less than $10^{-4}$ across the whole time interval.

5. Electron emission

With these developments of the embedding method, we turn to electron emission from the metal surface represented by the Cu(111) effective potential. As in section 4, we apply the time-dependent perturbation given by (29), keeping the width parameter $\Delta$ fixed at 2 au, but with varying amplitude and frequency. This models the perturbation due to $p$-polarized light when the $E$-field of the incident light has a large component normal to the surface, giving rise to surface photoemission [31]. We begin with emission from the continuum state at $E = 0.1$ au. Figure 7 shows the current $J_\delta$ emitted into the vacuum at $z_v = 20$ au at two frequencies of perturbation, $\omega = 0.4$ and 0.8 au; we use amplitudes of $A = 0.01$, 0.1 au at $\omega = 0.4$ au, and $A = 0.01$ au at $\omega = 0.8$ au. These results are calculated using an embedded region between ±20 au, with 70 basis functions defined with $2D = 44$ au. First the results for amplitude $A = 0.01$ au shown by solid lines in the figure: there is a time-delay before the current reaches $z_v$—we shall discuss this later—but after a large initial peak, the current shows oscillatory transients about a constant current. By curve-fitting (we fit a straight line to the time-integrated current $J_\delta$), we estimate that the average current after the initial peak is $1.0 \times 10^{-4}$ au for $\omega = 0.4$ au and $2.65 \times 10^{-5}$ au for $\omega = 0.8$ au. We can also calculate the long-term average current for small perturbations from Fermi’s golden rule [32, 33],

$$\bar{J}_\delta = \frac{1}{k_f} |\langle i | \delta V | f \rangle|^2,$$

(39)

where $|i\rangle$ is the initial state and $|f\rangle$ the final state, the time-reversed low-energy electron diffraction (LEED) state. $k_f$ is the wavevector of the final state (the incident free-electron wave in the LEED state is $\exp(-ikzc)$), coming from the density of final states in one dimension, $1/(2\pi k_f)$—the $2\pi$ cancels with the prefactor of $2\pi$ in the golden rule [22]. With $A = 0.01$ au the golden rule expression gives $\bar{J}_\delta = 9.62 \times 10^{-5}$ au for $\omega = 0.4$ au, and $\bar{J}_\delta = 2.65 \times 10^{-5}$ au for $\omega = 0.8$ au, in
agreement with the time-dependent calculations. The decrease in current with increasing frequency is due to a combination of density of states and matrix element effects, as we see from (39).

The lower the excitation frequency, the longer the period of the transients. The corresponding frequency is, in fact, close to the final state electron energy measured from the vacuum zero—thus, the transient frequency for $\omega = 0.8$ au is about 0.47 au, compared with the final state energy measured from the vacuum zero of 0.46 au. Suddenly switching on the perturbation gives rise initially to a range of energies of emitted electrons, starting at the vacuum zero, and it is the interference of these states with the long-term final state which gives rise to the transients.

Increasing the perturbation amplitude by a factor of 10 at $\omega = 0.4$ au, the current shows very pronounced oscillations of much shorter period on top of the transient oscillations (figure 7, dashed line). In fact even with $A = 0.01$ au, these short-period oscillations are visible. Comparing the current for $A = 0.01$ au multiplied by a factor of 100 with that for $A = 0.1$ au (figure 7, curves a), we see that the amplitude of the short-period oscillations is nonlinear in the intensity of the perturbation, varying as the cube of the perturbation amplitude $A$. This shows that these oscillations are the result of interference between first-order and second-order excitations from the bulk state; the frequency of the short-period oscillations is exactly 0.4 au, as we would expect with an interference term. From the amplitude of the interference term, confirmed by a Fourier analysis of the wavefunction at $z_v = 50$ au over an extended time interval ($0 < t < 800$ au), we estimate that the relative intensity of the second-order excitation is about 1% with $\omega = 0.4$ au and $A = 0.1$ au. The interference term in the current is much less pronounced in emission with the higher excitation frequency of $\omega = 0.8$ au—the excited electron moves rapidly away from the perturbation, before it can be further excited.

It is interesting to study the electron number $Q(t)$ in the embedded region, and its relation to the time-integrated currents across the bulk and vacuum embedding surfaces—we met $[Q(t) + J_e(t) + J_h(t)]$ in section 4. Figure 8 shows $Q(t)$, $J_e(t)$, and $J_h(t)$ for excitation from the continuum state with energy $E = 0.1$ au by the surface perturbation with $\omega = 0.8$ au and amplitude $A = 0.1$ au, and an embedded region between $z_e = -20$ au and $z_h = +20$ au. Both $Q(t)$ and $J_e(t)$ show persistent short-period oscillations due to crystal potential interference effects, but averaging these by eye we see that after an initial transient, $Q$ settles down to an almost constant value. This is the result of the current leaving the surface region into the vacuum across $z_e$ being balanced by the current approaching the surface from the bulk across $z_h$—the slopes of $J_e(t)$ and $J_h(t)$ are almost equal and opposite (remember, positive current means charge leaving the surface region). So in emission from a continuum state, the wavefunction is replenished from the bulk, and the electron number at the surface reaches a steady state.

The behaviour is quite different in emission from the Shockley surface state at $E = 0.2415$ au. Figure 9 shows the number of electrons in the surface region and time-integrated currents with $\omega = 0.6585$ au, giving the same final state energy as in figure 8, and $A = 0.1$ au. The electron number $Q$ drops steadily, as the surface state is depopulated by currents leaving the surface into the bulk as well as into the vacuum (in reality, many-body lifetime effects neglected here repopulate the surface state hole). The near-equality of $J_e(t)$ and $J_h(t)$ apparent in figure 9 approximately conserves momentum in the emission process, though the surface step also provides a source of momentum [31]. This contrasts with emission from
the continuum state, where momentum is directed from the bulk into the vacuum.

Finally we turn to the question of the time it takes for the emitted electrons to leave the surface. From the curves for \( j_z(t) \) shown in figure 7 it is clear that there is no unique time at which the electrons start to arrive at \( z_e \), where we measure the current—do we mean the time at which the current differs from zero, or perhaps when the first peak arrives? The first is ill-defined, as the increase from zero is gradual, and numerical limitations mean that we cannot fix it accurately. The second is too late, especially for the emission curves at short time.

However, we can define a convenient measure from the straight line fit to \( J_z(t) \), which we used to find the average current. Figure 10 shows the time-integrated current \( J_z(t) \) evaluated at \( z_e = 20 \) au in emission from the continuum state with \( E = 0.1 \) au, excited by the surface perturbation with frequency \( \omega = 0.8 \) au and amplitude \( A = 0.01 \) au, fitted by a straight line beyond \( t = 80 \) au. We define the effective arrival time \( t_e \) for the current as the intercept of the linear fit with the time axis—in this case, \( t_e = 18.3 \) au after switching on the perturbation at \( t = 0 \) au. This compares with the classical arrival time of 20.8 au, evaluated with electrons starting at \( z = 0 \) au and travelling with the final state velocity. Figure 11 shows \( j_z(t) \) measured at different values of \( z_e \), together with the arrival times \( t_e \) determined from the linear fits: we see that our effective arrival times lie close to the start of the steep initial rise in current. The classical arrival times are about 2 au later, still not long after the start of the current rise, and well before the first peak.

We can extend these arrival time results by shifting the excitation potential into the solid, displacing the time-dependent perturbation (29). Table 2 shows the extra time for electrons to arrive at \( z_e = 50 \) au, evaluated from the linear fit to the current, and also classically from the electron velocity inside the solid. There is excellent agreement, confirming the picture that even at relatively low final state energies, electron emission proceeds via excitation into a wavepacket at the point of perturbation.

6. Conclusions

We have shown that our time-dependent embedding method is very accurate, but ultimately there is the problem that the time for evolving the wavefunction through \( \delta t \) is very accurate, but ultimately there is the problem that the time for evolving the wavefunction through \( \delta t \) is proportional to \( t \)—the embedding integral in the Hamiltonian has an upper limit of \( t \) (17). On the desktop computer on which the present calculations are performed, our longest calculations so far go up to a time of 800 au (about 20 fs), and to reach much longer times further developments of the method are necessary. Moreover, the calculations described here only involve a single electron, and we must include electron–electron interaction effects, initially at the self-consistent level. In the meantime there is much to do with the existing surface programmes, considering excitation by ultra-short light pulses, multi-photon processes and the like. Our time-dependent embedding method should have other applications, for example to adsorbates [34] and metallic contacts [35], where time-independent embedding has proved useful.

Acknowledgments

I would like to thank S Crampin and M I Trioni for their help.

References

[1] Cavalieri A L et al 2007 Nature 449 1029–32
[2] Landauer R and Martin T 1994 Rev. Mod. Phys. 66 217–28
[3] de Carvalho C A A and Nussenzveig H M 2002 Phys. Rep. 364 83–174
[4] Miaja-Avila L, Saathoff G, Mathias S, Yin J, La-o-vorakiat C, Bauer M, Aeschlimann M, Murnane M M and Kapteyn H C 2008 Phys. Rev. Lett. 101 046101
[5] Inglesfield J E 2008 J. Phys.: Condens. Matter 20 095215
[6] Kazansky A K and Echenique P M 2009 Phys. Rev. Lett. 102 177401
[7] Kazansky A K and Echenique P M 2010 Phys. Rev. B 81 075440
[8] Kulander K C, Schafer K J and Krause J L 1991 Phys. Rev. Lett. 66 2601–4
[9] Hellums J R and Frensley W R 1994 Phys. Rev. B 49 2904–6
[10] Ehrhardt M 1999 VLSI Des. 9 325–38
[11] Inglesfield J E 1981 J. Phys. C: Solid State Phys. 14 3795–3806
[12] Benesh G A and Inglesfield J E 1984 J. Phys. C: Solid State Phys. 17 1595–606
[13] Ishida H 2001 Phys. Rev. B 63 165409
[14] Boucke K, Schmitz H and Kull H J 1997 Phys. Rev. A 56 763–71
[15] Majica V, Nitzan A, Datta S, Ratner M A and Kubiat C P 2003 J. Phys. Chem. B 107 91–5
[16] Baraff G A and Schlüter M 1986 J. Phys. C: Solid State Phys. 19 4383–91
[17] Dirac P A M 1930 Proc. Camb. Phil. Soc. 26 376–85
[18] Frenkel J 1934 Wave Mechanics, Advanced General Theory (Oxford: Clarendon)
[19] Chulkov E V, Silkin V M and Echenique P M 1997 Surf. Sci. 391 L1217–23
[20] Chulkov E V, Silkin V M and Echenique P M 1999 Surf. Sci. 437 330–52
[21] Echenique P M, Berndt R, Chulkov E V, Fauster T, Goldmann A and Höfer U 2004 Surf. Sci. Rep. 52 219–317
[22] Merzbacher E 1998 Quantum Mechanics 3rd edn (New York: Wiley)
[23] Inglesfield J E 2001 Comput. Phys. Commun. 137 89–107
[24] Inglesfield J E 2010 arXiv:1003.2282
[25] Butti G 2005 PhD Thesis Università degli Studi di Milano-Bicocca
[26] Kohn W 1959 Phys. Rev. 115 809–21
[27] Olver F W J, Lozier D W, Boisvert R F and Clark C W (ed) 2010 NIST Handbook of Mathematical Functions (Cambridge: Cambridge University Press)
[28] Thompson I J and Barnett A R 1986 J. Comput. Phys. 64 490–509
[29] Jurczyszyn L 1991 Surf. Sci. 259 65–9
[30] Thijssen J M 1999 Computational Physics 1st edn (Cambridge: Cambridge University Press)
[31] Levinson H J, Plummer E W and Feibelman P J 1979 Phys. Rev. Lett. 43 952–5
[32] Feibelman P J and Eastman D E 1974 Phys. Rev. B 10 4932–47
[33] Hermeking H and Wehrum R P 1975 J. Phys. C: Solid State Phys. 8 3468–75
[34] Achilli S, Trioni M I, Chulkov E V, Echenique P M, Sametoglu V, Pontius N, Winkelmann A, Kubo A, Zhao J and Petek H 2009 Phys. Rev. B 80 245419
[35] Ishida H 2008 Phys. Rev. B 77 155415