The Theory of Diffraction in Electron Stimulated Desorption

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# Introduction

Materials modification by electron beams and the desorption of surface-bound species induced by electronic transitions (DIET) are phenomena of both fundamental and technological interest, including electron-beam induced processes in materials growth and etching, lithography, hot-electron induced defects in devices, radiation damage, stimulated catalysis, and even astrophysics. Stimulated desorption is also a concern for damage effects when attempting traditional surface probes such as photoemission, low-energy electron diffraction, and electron microscopy on radiation-sensitive materials, such as oxides and molecular solids. One issue central to understanding stimulated desorption is the relationship between the atomic and electronic structure of a surface species and its desorption probability.

In our recent article “”, we describe experiments demonstrating that total electron-stimulated desorption (ESD) yields are a function of incident electron direction, due to quantum-mechanical scattering and interference of the incident electron to form a surface standing wave in the initial state of the desorption process. This electron standing wave exhibits spatially localized maxima and minima in the electron density. Whether a particlar site on a surface experiences a maximum or a minimum depends on the energy (wavelength) and direction of incidence of the electron, and the arrangement of nearest-neighbor atoms surrounding the site. Since the probability of desorption is proportional to the incident electron density at the site of the “absorber” (the site of the excitation which leads to desorption), the total yield depends upon the local atomic structure and the k-vector of the incident wave. Comparison of experimental data to theoretical calculations can then reveal the atomic bonding geometry of the surface site involved in desorption, and the atomic site whose excitation is responsible for initiating the desorption process. Measurements made in this way reveal information about the desorption complex with sub-angstrom resolution of bond vectors. This Electron Standing-Wave Stimulated Desorption (ESWSD) technique makes possible a new surface spectroscopy with diverse applications. The ESWSD technique is especially useful for surface characterization of radiation-sensitive materials, such as oxides, salts, and molecular solids. ESWSD is a general technique, applicable to any system exhibiting ESD, and combines the chemical sensitivity of secondary-ion mass spectrometry with the structural sensitivity of LEED or photoelectron diffraction. .

ESWSD is not a passive structural characterization technique, since material is actively removed from the surface during analysis. In our paper, we demonstrate that it is, at least in principle, possible to selectively desorb atoms from specific surface bonding. The applications of such a capability are numerous. Besides the obvious utility in the basic sciences, it may be possible to manipulate the growth of materials to produce surfaces having unique structural properties. For some systems, growth proceeds only on areas of the surface on which a chemical passivation layer has been removed. ESWSD makes it possible, in theory, to remove passivation preferentially on selected atomic sites, and therefore to stimulate different growth modes, depending on the energy and direction of an incident electron beam. Changing the incident electron energy or direction may then allow growth to be "switched" between different modes. Such a capability does not now currently exist, and would represent a tremendous advance in our ability to manipulate materials on the atomic scale. To demonstrate this capability, we propose to use ESWSD to control the growth mode of silicon surfaces in a chemical vapor-deposition (CVD) environment.

Structural characterization of surfaces is, of itself, nothing new. However, given the importance of stimulated desorption, very little is known concerning the relationship between the structure of a surface and its sensitivity to ESD. Previous studies have examined ion desorption trajectories, related to initial state bonding geometry because desorption trajectories typically follow bond axes. While these studies have been successful in measuring the bonding geometry of several adsorbate systems, it is a semi-quantitative probe at best, and gives no information regarding bond distances or nearest-neighbor atom locations. As a consequence, ESD has not been a widely utilized probe of surface structure, when compared to other surface spectroscopies, and the structure-function relations involved in desorption are poorly understood. In addition to information about surface structure, ESWSD is potentially a very powerful technique for illuminating the relationship between localized states and excitations leading to desorption.

# Theory of DESD

## Derivation of the desorption rate equations

The rate *R* at which atoms or molecules of a particular chemical species leave the surface can be expressed as a simple product of the incident electron flux *I*, the probability that an incident electron will cause an excitation which could potentially lead to desorption, and the total probability *D* that the excitation results in a desorbate escaping the surface.

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In the most general case, there may be multiple types of excitations giving rise to multiple desorption channels, and the total rate is the sum of the rates of the individual channels *j*:

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For any one desorption channel, the time-independent excitation rate is given by Fermi’s Golden Rule:

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Where the labels *i* and *f* denote the initial and final states of the system, respectively (including the incident electron and any outgoing ionization electrons, assuming the desorption is triggered by an ionization event. In general, the final state could include non-ionized excited states such as plasmons or phonons), and is the density of final states.

The transition probability is proportional to the square of the integral of the interaction over all of the space appropriate to the problem:

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Several qualities of this integral make it very challenging to calculate:

* the electron-electron interaction is a long-ranged Coulomb interaction, necessitating integration over a large volume (potentially extending to the entire solid)
* the final state can be complex, with one or more outgoing electrons, holes, and/or quasiparticles, and many possible degenerate channels

These complexities notwithstanding, there are several features of ESD that allow us to make various simplifying approximations. First, approximate the initial state wave function as the simple product of the wave functions of the (ground state) solid and the incident electron moving in the potential of the solid:

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Giving

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Assuming a one-electron interaction:

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The magnitude of the rate difference between two adjacent incident vectors k1 and k2 is:

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In this approximation the initial state is given by the anti-symmetric Slater determinant:

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Within the muffin-tin potential, exchange is approximated by the Slater approximation when solving for Psi1, and includes the exchange interaction with the target electron. So we will ignore the exchange integral contribution.

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The initial-state interaction between the incident electron and the solid will be comprehended in the Hartree-Fock-Slater approximation, in which the incident electron moves in the total field of the other *N* electrons and ion cores, and includes exchange in the Slater approximation.

Assumptions:

* ESD occurs due to a *single* *electron* excitation event predicated by an interaction with the incident electron.

Assuming that the incident flux is constant, and that the probability of desorption is constant (for a given incident electron energy),

We shall make several assumptions to radically simplify the problem, while retaining the essential physics of interest:

We shall ignore the details of the final state (radiative & non-radiative core hole relaxation, Auger decays, etc)

Our experiment is focusing on the dependence of the total ESD rate on the incident electron direction and not energy. The energetic of the interaction is constant, so we care only about those components of the interaction which depend on k-hat.

Let’s assume that the interaction is between two electrons only, both moving in the potential of the solid (and are eigenfunctions of the potential of the solid)

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We assume that the incident electron is described by the wave function and that the “target” electron is in a (negative energy) bound state of the “target” atom .

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Where the interaction Hamiltonian is a screened Coulomb potential with screening length .

If we further assume that anddo not depend on ,(this is not necessarily true, but we rely upon the integration to make the assertion not too false), then the final state integral can be replaced by a constant term:

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The target electron wave function is essentially zero outside of the muffin-tin radius, so the limits of integration become:

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Now we further approximate that the screening length , and the majority of the contribution to the excitation rate

If we replace the Coulomb potential with its multipole expansion:

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The target wavefunction is expressed in terms of spherical harmonics and the radial wave functions:

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Subbing all of these in,

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Since the orthogonality of the spherical harmonics states that

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Then the expression above simplifies to

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(Take this further – the phi is expressed in an expansion of spherical waves about the absorber) – you’ll get another Ylm and Rlm

To a first approximation, the likelihood of a deep core excitation event is proportional to the amount of incident electron charge in the near vicinity of the core state (i.e, within the muffin-tin radius). While final-state effects dependent on the details of the outgoing electron k-vectors will have some structure effects, these will be treated as higher order corrections.

Strategy – what would the equations be in a time-reversed picture? If I picture waves of pure angular momentum l radiating outwards from the (absorber) atom (analogous to the photoemission process without the optical interaction and the core hole), scattering through the solid and then propagating to the detector, I’d expect to see some amplitude arrive there, corresponding to the amplitude placed into that l-state of the absorber if time is reversed. If I do this for all angular momenta and sum (coherently?), that should be proportional to the total amplitude, and therefore the total charge density.

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The incident electron in the solid satisfies the Schrodinger equation

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The Hamiltonian is given by

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Where

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Is the kinetic energy operator (free space Hamiltonian), and the energy in the solid is adjusted for the inner and optical potentials:

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is the free space energy (the incident electron beam energy).

The wave function of the incident electron within the (spherically symmetric) absorber muffin-tin is given by the expansion in terms of the radial wave functions and the spherical harmonics:

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We will make the assertion that, all other things being equal, the probability of ionization of the target atom (leading to subsequent desorption) is proportional to the total incident electron charge density in the vicinity of the core level, i.e., within the muffin-tin.

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The associated homogenous equation is

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Which has the solution

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Note that, for complex E, the wave vector k is also complex, and the plane wave solutions decay.

For the general solution, we begin by operating on both sides of Eq. 30:

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The full solution of Eq. 30 is the particular solution plus the general solution:

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Since the operator 1 / (E – H0) is divergent, we move the poles onto the imaginary axis by adding a factor of , with the understanding that we will take the limit at the end of it all.

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We define the Green’s operator G as

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Let’s think a bit. What I want to know is the wave function in the vicinity of the absorber atom

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Since

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In an r-basis:

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To within, I believe, a normalization factor. CHECK THIS.

I could consider the time-reversed problem and look at spherical outgoing waves from the origin of pure angular momentum, scattering to outgoing plane waves. The sum of all L for the spherical waves would give a set of phased plane waves that would interfere and produce a total outgoing amplitude. I actually kind of like this approach.

Now, the wave function outside of the muffin tin is given by:

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Projecting this function onto the spherical wave basis:

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The inner integral

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Subbing:

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Let’s isolate the integrals over r:

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I’m not absolutely sure of this, but I \*think\* the normalization of the wave functions is such that it is always real (this is what we assume when calculating the phase shifts – the imaginary terms (those involving yn) drop out. If this is the case in general, then we can ignore the contribution to the wave function from the spherical Bessel function of the second kind, and we get:

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|  |  |

And therefore

|  |  |
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Note that if we defined the spherical wave basis set without the factor of i^l, this would give back the exact same thing we started with. Let’s try that:

Going back to the start:

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|  |  |

Orthonormality of the spherical wave basis:

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Works just fine. This also passes the completeness test.

Now, the wave function outside of the muffin tin is given by:

|  |  |
| --- | --- |
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Note that the spherical Bessel function of the first kind is the real part of the spherical Hankel function. SO – this works, and the outgoing spherical wave is identical to:

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Also note that

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Hmm. This’d be “neater” if it was sin, like in the t-matrix.

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I wonder… does the factor of 2i come from the calculation of the t-matrix in the angular momentum basis?

Going back a few steps:

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Zoom in on the last integral:

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I have a sneaking suspicion that the imaginary part is zero.

# Solution of Atomic Wavefunctions

The radial Hartree-Fock equations are:

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Where the *Pi*(*r*) are the *r*-multiplied radial wave functions

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Which are normalized such that

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The volume integral of the *Rn,l*(*r*) wave functions is the total charge:

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Define the exchange potential *Vex*(*r*) as:

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| --- | --- | --- |
|  |  |  |

Define the full potential *V*(*r*):

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| --- | --- | --- |
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Substituting into (1) gives:

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| --- | --- | --- |
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Multiply through by -2*m*/ *ħ*2:

|  |  |  |
| --- | --- | --- |
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In Rydberg units (*ħ* = 2*m*e = *e*2/2 = 1), the radial equation is:

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| --- | --- | --- |
|  |  |  |

Where

|  |  |  |
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## The Method of Herman and Skillman

In the central field approximation (following Herman and Skillman),

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|  |  |  |

Where the radial charge density is

|  |  |  |
| --- | --- | --- |
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And the spherically averaged radial charge density is

|  |  |  |
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Note the form of the exchange potential *Vex*(*r*)

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The r-multiplied radial potential *U*(*r*) is

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The r-multiplied exchange potential is:

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| --- | --- | --- |
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Substituting sigma for rho:

|  |  |  |
| --- | --- | --- |
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In the central field approximation (following Herman and Skillman),

|  |  |  |
| --- | --- | --- |
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Where the radial charge density is

|  |  |  |
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Where *Nnl* is the occupation number for the orbital (n,l) with both spins, and the spherically averaged radial charge density is

|  |  |  |
| --- | --- | --- |
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Note that the free-electron approximation for the exchange potential exactly cancels out the self-potential due to the electron, so that the radial charge density includes contribution from all electrons, including the one whose wave function is being solved for.

Since the functions s(r) and p(r) are both negative, they form repulsive (positive) potential terms. The nuclear potential and the exchange potential terms are both attractive (negative).

## Latter Tail Correction

The correct potential to use in Eq 1 is slightly modified from that given in Eq 4:

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Where Z is the atomic number and N is the number of electrons. The switching radius *r*0 is chosen such that

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## V(r) function for Numerov

The differential equation to solve is:

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Numerov’s method is useful for solving DEs of the form:

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When expressed in this form, the Numerov function *v*(*r*) is:

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Note that since *V*(*r*) is only a function of the total radial charge densities summed over n and l, it does not need to be modified as E changes or as the identity of the electron orbital being computed changes. E can be changed independently, which is very convenient for the energy eigenvalue solver.

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## Solving for *Pnl*(*r*) with Numerov’s algorithm

Numerov’s method is useful for solving DEs of the form:

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| --- | --- | --- |
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In our case,

With the additional boundary conditions that

{need another boundary condition here to ensure unique solution to within a constant}

Which can be numerically solved using Numerov’s method. On a uniform mesh of spacing *h =* (*rn+1 – rn*),

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Integration in the backward direction is symmetric with respect to the indices:

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If the interpoint spacing is non-uniform such that

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Equation (19) reduces to Eq(17) when *a* = *b*. Integration in the backward direction is *not* symmetric with respect to the indices:

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I’m not sure the non-uniform spacing equation is right – you’d think it should be symmetric with respect to interchange of a and b, but it is not – the primary issue are the + (*a*2 + *ab* – *b*2) and the – (*a*2 – *ab* – *b*2) terms – both of these just happen to reduce to + *h*2 when *a* = *b* = *h* and so give the proper limit, but they are not symmetric with respect to interchange of *a* and *b*.

# Rydberg Units

The Rydberg

The Bohr radius

Calculating muffin-tin potentials:

<http://hermes.phys.uwm.edu/projects/elecstruct/mufpot/MufPot.TOC.html>

# Inner Potential and Refraction Effects

If we define the inner potential boundary surface to be a plane perpendicular to the z-axis, located at , then the total distance the incident electron (plane wave) travels in the solid before scattering is

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Where

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The incident electron experiences an amplitude degradation due to the optical potential, of magnitude:

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# Finite Difference Estimates of Derivatives

## Discrete approximation for the first derivative:

The definitions of the one-sided discrete derivatives are:

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The “centered approximation” is the average of the one-sided derivatives:

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For a uniform mesh (*δx* is a constant = *h*), the centered approximation reduces to:

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### Taylor series expansions

In order to connect the finite-difference approximations of derivatives to analytical derivatives, we make use of the Taylor series expansion about the point *x*,

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An estimate of the error in the finite difference approximation can be had by substituting the Taylor expansions of *u*(*x* ± *h*) into the expressions for *D±u*:

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From these expressions, it can be seen that the expected deviation from the true value of the first derivative is dominated by the first term in *h*, meaning that the error is of first order in *h.*

The usefulness of the centered approximation is due to the alternating signs of the odd order terms in Eqs 7 and 8, which cause these terms to cancel out produce an estimate good to second order in *h*:

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### Non-uniform mesh

For the more general case of a non-uniform mesh, the cancellation of terms in the centered approximation does not occur:

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Here we have defined *h*+ = (*xi* + 1 – *xi*) and *h*– = (*xi* – *xi* – 1). In this case, the error is dominated by a term on the order of the difference in size of adjacent mesh points *h*+ – *h*– = *xi* + 1 – 2*xi* + *xi* – 1.

Rearranging terms to isolate the first derivative,

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Expanding out to higher orders in u,

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## Discrete approximation of the 2nd derivative:

The centered approximation for the second derivative is

|  |  |  |
| --- | --- | --- |
|  |  |  |

Here we have introduced the notation *u*+ = *ui* + 1, *u*– = *ui* – 1, and *u*0 = *ui*. In the case of a uniform mesh, this reduces to

|  |  |  |
| --- | --- | --- |
|  |  |  |

Substituting the Taylor expansions into the uniform mesh case, we arrive at the error estimate:

|  |  |  |
| --- | --- | --- |
|  |  |  |

showing that this estimate in the 2nd derivative is good to second order in *h*. Simple rearrangement of the expression gives

|  |  |  |
| --- | --- | --- |
|  |  |  |

### Non-uniform mesh

|  |  |  |
| --- | --- | --- |
|  |  |  |

In the limit of a symmetric mesh, Eq. 15 reduces to Eq, 13. Reducing Eq. 15 to an expression for the second derivative gives

|  |  |  |
| --- | --- | --- |
|  |  |  |

Showing that the error in the 2nd derivative for a non-symmetric mesh is on the order of the size of adjacent mesh points *h*+ – *h*– = *xi* + 1 – 2*xi* + *xi* – 1, the same as for the first derivative. In the limit of a symmetric mesh, Equation 16 reduces to Eq. 14.

## Generalized Numerov’s Method

Given a differential equation of the form:

|  |  |  |
| --- | --- | --- |
|  |  |  |

We wish to obtain a finite-difference solution of this equation that is usable on an arbitrary mesh. If we define and apply the finite-difference approximation for the second derivative, we obtain

|  |  |  |
| --- | --- | --- |
|  |  |  |

For the rest of this section, we will adopt the notation *a* = *h*+, *b* = *h*–.

|  |  |  |
| --- | --- | --- |
|  |  |  |

If we then replace the first and second derivatives of *F* with centered difference approximations, and *F* with its definition:

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

Substituting for the first derivative and simplifying as we go,

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

Substituting in for the second derivative:

|  |  |  |
| --- | --- | --- |
|  |  |  |

Gathering terms on *F*,

|  |  |  |
| --- | --- | --- |
|  |  |  |

Now substituting in the definitions of *F*:

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

To arrive at a recursion relation we gather terms on *y*+

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

As a quick check, let’s see what this reduces to in the limit that *a* = *b*:

|  |  |  |
| --- | --- | --- |
|  |  |  |

Which is correct!

Let’s go back to Eq. 23.10 and further collect terms, we arrive at our final expression for Numerov’s algorithm on a generic mesh:

|  |  |  |
| --- | --- | --- |
|  |  |  |

In the special case where *u*(*x*) = 0 (as is true for the Schrodinger equation), this expression reduces to

|  |  |  |
| --- | --- | --- |
|  |  |  |

Again checking in the limit that *a* = *b* = *h*,

|  |  |  |
| --- | --- | --- |
|  |  |  |

Which again is correct.

What is very odd is that the earlier expression I derived for the non-uniform mesh is NOT equivalent to this expression, but does reduce to exactly the same thing in the limit that *a* = *b*.

## Earlier results





When *u*(*x*) = 0,

|  |  |  |
| --- | --- | --- |
|  |  |  |

Note that the expression in Eq. 25 is NOT the same.

## Calculating y1

In order to apply this recursion relation, it is necessary to know the values of *y*0 and *y*1. If *y*1 is not known *a priori*, it can be computed if the first derivative of *y* is known:

|  |  |  |
| --- | --- | --- |
|  |  |  |

In our case,

|  |  |  |
| --- | --- | --- |
|  |  |  |

Using the definition of F utilized in Eq. 19,

|  |  |  |
| --- | --- | --- |
|  |  |  |

Similarly,

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

Substituting Eq. 32 into Eq. 30 gives

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

Substituting for F,

|  |  |  |
| --- | --- | --- |
|  |  |  |

Collecting terms on *y*+,

|  |  |  |
| --- | --- | --- |
|  |  |  |

If *u* = 0,

|  |  |  |
| --- | --- | --- |
|  |  |  |

which matches Numerov’s result.

When y0 = 0,



I suggest starting with a guess for y’ and normalizing after-the-fact. Later on, I can look up what y’ is experimentally and optimize the guess.

### Starting backward integration

In order to apply this recursion relation, it is necessary to know the values of *y*N and *y*-. If *y*- is not known *a priori*, it can be computed if the first derivative of *y* is known:

|  |  |  |
| --- | --- | --- |
|  |  |  |

In our case,

|  |  |  |
| --- | --- | --- |
|  |  |  |

Using the definition of F utilized in Eq. 19,

|  |  |  |
| --- | --- | --- |
|  |  |  |

Similarly,

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

Substituting Eq. 42 into Eq. 40 gives

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

Substituting for F,

|  |  |  |
| --- | --- | --- |
|  |  |  |

Collecting terms on *y*-,

|  |  |  |
| --- | --- | --- |
|  |  |  |

If *u* = 0,

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

When *yN* = 0,

|  |  |  |
| --- | --- | --- |
|  |  |  |

I suggest starting with a guess for y’ and normalizing after-the-fact. Later on, I can look up what y’ is experimentally and optimize the guess.

## Partial Wave Scattering Theory

From Pendry:

The phase shifts can be calculated by integration of the Schrodinger equation starting at the origin, where we have the boundary condition that the wave function must not be singular, and proceeding out to the boundary of the muffin-tin sphere. Once out of range of the potential we know that the wave function has the form:

|  |  |  |
| --- | --- | --- |
|  |  |  |

The r-multiplied wave function has the form:

|  |  |  |
| --- | --- | --- |
|  |  |  |

And has the derivative:

|  |  |  |
| --- | --- | --- |
|  |  |  |

And from details of the integration we calculate the logarithmic derivative at the boundary of the muffin-tin sphere, radius *R*,

|  |  |  |
| --- | --- | --- |
|  |  |  |

The logarithmic derivative for the r-multiplied wave function is:

|  |  |  |
| --- | --- | --- |
|  |  |  |
|  |  |  |
|  |  |  |

Solving eq. 2 for the exponential including the phase shift,

|  |  |  |
| --- | --- | --- |
|  |  |  |

Or

|  |  |  |
| --- | --- | --- |
|  |  |  |

If we know the phase shifts for a real energy E, we can compute the (complex) phase shift for the imaginary energy E (including the optical potential) as follows:

|  |  |  |
| --- | --- | --- |
|  |  |  |

Calculation of the spherical Hankel functions:

|  |  |  |
| --- | --- | --- |
|  |  |  |
|  |  |  |

Where the and are the spherical Bessel functions.

According to Wikipedia,

|  |  |  |
| --- | --- | --- |
|  |  |  |

Inside the muffin-tin sphere, we can decompose the incident electron wave function into its partial waves

|  |  |  |
| --- | --- | --- |
|  |  |  |

The phase shifts can be calculated by integration of the Schrodinger equation starting at the origin, where we have the boundary condition that the wave function must not be singular, and proceeding out to the boundary of the muffin-tin sphere. Once out of range of the potential we know that the wave function has the form:

|  |  |  |
| --- | --- | --- |
|  |  |  |

The r-multiplied wave function has the form:

|  |  |  |
| --- | --- | --- |
|  |  |  |

And has the derivative:

|  |  |  |
| --- | --- | --- |
|  |  |  |

And from details of the integration we calculate the logarithmic derivative at the boundary of the muffin-tin sphere, radius *R*,

|  |  |  |
| --- | --- | --- |
|  |  |  |

The logarithmic derivative for the r-multiplied wave function is:

|  |  |  |
| --- | --- | --- |
|  |  |  |
|  |  |  |
|  |  |  |

Solving eq. 2 for the exponential including the phase shift,

|  |  |  |
| --- | --- | --- |
|  |  |  |

Or

|  |  |  |
| --- | --- | --- |
|  |  |  |

Alternate form – assume the wave function in the zero potential region has the form (from <http://galileo.phys.virginia.edu/classes/752.mf1i.spring03/Scattering_II.htm>):

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |

Rearranging to solve for terms in delta l,

|  |  |  |
| --- | --- | --- |
|  |  |  |

If we know the phase shifts for a real energy E, we can compute the (complex) phase shift for the imaginary energy E (including the optical potential) as follows:

|  |  |  |
| --- | --- | --- |
|  |  |  |

## Temperature Effects

The phase shift is further modified to include temperature effects.

|  |  |  |
| --- | --- | --- |
|  |  |  |

K is the electron momentum = sqrt(E) in Rydberg units.

Where

|  |  |  |
| --- | --- | --- |
|  |  |  |

(I am assuming the L = l,m)

|  |  |  |
| --- | --- | --- |
|  |  |  |

Alpha has units of 1/E. Here I’m using the symbol to represent the Debye temperature, m is the mass of the atom in electron mass units, kb is Boltzmann’s constant in Hartrees/Degree Kelvin, T is temperature in Kelvin. In Rydberg units (*ħ* = 2*m*e = *e*2/2 = 1), and Eq 17 is:

|  |  |  |
| --- | --- | --- |
|  |  |  |

Where M is the (dimensionless) ratio of the mass of the atom to the mass of the electron.

Kb has units [Energy/K] = 3.166815E-6 Hartrees/K

Since 1 Hartree = 27.211 eV = 2Ry, Kb = 6.33363E-6 Ry/K

|  |  |  |
| --- | --- | --- |
|  |  |  |

* Need to find out what phase convention for Ylm Pendry is using.

On the atomic mass term: M is the mass of the atom in electron mass units. For example, for Si, atomic weight is 28.0855 g/mol. The electron mass is 9.10938215x10-31 kg. Avogadro’s constant is 6.022142E23/mol. So the mass of a Si atom is 28.0855 [g/mol] / 6.02143E+23 [mol-1] = 4.66425E-23 g or 4.66425E-26 kg. In electron mass units this is 4.66425E-26 / 9.10938215E-31 = 5.12027E+4, which is a dimensionless number.

## Constructing the muffin-tin potential:

We will follow the method outlined for the MUFPOT program, <http://hermes.phys.uwm.edu/projects/elecstruct/mufpot/MP/MP.Theory1.html>.

The strategy with this method is to start with the tabulated wave functions of Herman and Skillman, compute from those the electron density , and then to solve the Poisson equation to determine the potential due to that charge density. The resulting electron potential is added to the nuclear coulomb potential and an exchange term (Slater approximation with statistical factor), and then the Mattheiss prescription is invoked to construct the muffin-tin.

The starting point is the set of free atom radial wave functions tabulated by the Atom class. The (spherically symmetric) electron density can be written:

|  |  |  |
| --- | --- | --- |
|  |  |  |

Note that this expression assumes the occupancy for a closed subshell (2l + 1).

It is relatively straightforward to compute the total radial electronic charge density from the Herman Skillman wavefuntions encapsulated in the Atom class.

* Atom should expose a method to retrieve rho(r).

Once we’ve got rho, the next step is to compute the contribution to the scattering potential due to it:

|  |  |  |
| --- | --- | --- |
|  |  |  |

Where the first term is the contribution from the nucleus and the second term is the electronic contribution defined by:

|  |  |  |
| --- | --- | --- |
|  |  |  |

Since and depend only on the radial coordinate r, we need only the radial part of the Laplacian. This allows us to redefine Eq. 13 to

|  |  |  |
| --- | --- | --- |
|  |  |  |

For a given , this equation can be solved for .

Complication – what about near the origin? Do we work instead with r \* rho and r \* u?

And I don’t think we need to do this anyway – I think the potential as given by Herman and Skillman \*is\* the right one to use.

Now I believe that the Herman Skillman potential is the right one to use EXCEPT for the fact that the exchange term in HS compensates for the self-charge of the single electron. The exchange potential in Herman and Skillman is:

|  |  |  |
| --- | --- | --- |
|  |  |  |

In comparison, the exchange term from Pendry is

|  |  |  |
| --- | --- | --- |
|  |  |  |

Where alpha is the statistical exchange parameter and is about 0.7.

Now I wonder if the extra factor of two in Herman-Skillman is due to the units used? Yes, it is – according to the documentation of the HS code,

|  |  |  |
| --- | --- | --- |
|  |  |  |

And in Rydberg units, *e*2 = 2. SO – it appears that the HS potential IS the right one to use, excepting that it does not include the effect of the incident electron on all of the others – which none of the methods does comprehend.

Theory (following <http://hermes.phys.uwm.edu/projects/elecstruct/mufpot/MP/MP.Theory1.html>)

We begin with the set of free atom radial wave functions taken from Herman and Skillman. For a closed subshell (electron occupancy ), the (spherically symmetric) electron density can be written

|  |  |  |
| --- | --- | --- |
|  |  |  |

This is normalized by the condition (extra factor of 2 due to electron spin)

|  |  |  |
| --- | --- | --- |
|  |  |  |

Where is the number of electrons in the subshell. The total electron charge density due to all electrons in the atom is

|  |  |  |
| --- | --- | --- |
|  |  |  |

The point of the process is to construct the potential arising from the nuclear charge, the electron cloud, and any overlapping charge from nearest-neighbor atoms.

|  |  |  |
| --- | --- | --- |
|  |  |  |

Where is the potential due to the charge density , found by solving the Poisson equation:

|  |  |  |
| --- | --- | --- |
|  |  |  |

Since and depend only on the radial coordinate, we need only the radial part of the Laplacian:

|  |  |  |
| --- | --- | --- |
|  |  |  |

And thus Poisson’s equation becomes:

|  |  |  |
| --- | --- | --- |
|  |  |  |

For a given density, this equation can be solved for the potential.

The next step is to superimpose the spherically-symmetric potentials of neighboring atoms to find the muffin-tin potential at any particular atom. We do this by expanding the potential for atom n about the origin (assumed to be at the center of the muffin-tin atom) in terms of spherical harmonics:

|  |  |  |
| --- | --- | --- |
|  |  |  |

The zeroth order spherically symmetric component of the potential of atom n referenced about the origin (at a distance a from the origin) is:

|  |  |  |
| --- | --- | --- |
|  |  |  |

And therefore the total spherically symmetric coulomb potential of the muffin-tin is

|  |  |  |
| --- | --- | --- |
|  |  |  |

Where is the distance from the origin of the muffin tin to the origin of the nearest-neighbor atom n (bond distance).

In a similar fashion, contributions to the Slater exchange potential due to nearest-neighbor atoms will be

|  |  |  |
| --- | --- | --- |
|  |  |  |
|  |  |  |

And the total spherically symmetric potential of the muffin-tin, including exchange, is

|  |  |  |
| --- | --- | --- |
|  |  |  |

Practical implementation:

As increases, the relative contribution to the central potential decreases rapidly. In practice it should not be necessary to sum over more than 1 or 2 nearest-neighbor shells. Potentials derived by this method will be site-dependent, especially in that surface atoms will have a different potential than bulk, which gives a better approximation of reality than Pendry muffin-tin potentials.

# The Separable Propagator Technique of Rehr and Albers

The cl(rho) are the dimensionless polynomial factors that multiply the asymptotic (meaning, here, the series expansion) form of the spherical Hankel function:

|  |  |
| --- | --- |
|  |  |

The series expansion is:

|  |  |
| --- | --- |
|  |  |

therefore

|  |  |
| --- | --- |
|  |  |
|  |  |

And

|  |  |
| --- | --- |
|  |  |

Hmmm… Interesting. Rehr says he’s adopted throughout the convention of Messiah for spherical Bessel functions, spherical harmonics, Legendre polynomials, and rotation matrices. What does Messiah say about h?

AhHA – Messiah has a different phase convention for spherical Bessel functions than what I’ve been using. WONDERFUL.

## Messiah Convention

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |
|  |  |

Rehr and Albers give

|  |  |
| --- | --- |
|  |  |

And so

|  |  |
| --- | --- |
|  |  |

Having specific values

|  |  |
| --- | --- |
|  |  |
|  |  |

Which matches Rehr.

## Standard Convention

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |
|  |  |

And the Cl(rho) have the same definition as Messiah, if we keep the imaginary multiplier out front.

|  |  |
| --- | --- |
|  |  |

Asymptotic forms of the spherical Bessel functions:

|  |  |
| --- | --- |
|  |  |

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| --- | --- |
|  |  |

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| --- | --- |
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Asymptotic form of the spherical Hankel function of the first kind:

|  |  |
| --- | --- |
|  |  |

## Derivation of the Separable Representation of the Propagator

|  |  |
| --- | --- |
|  |  |

Where k is the free particle kinetic energy. Note that rho is dimensionless.

The dimensionless outgoing free propagator is

|  |  |
| --- | --- |
|  |  |

We expanding this in terms of spherical waves about the fixed sites **R** and **R**’ by inserting complete sets of states:

We have defined the displaced spherical wave basis such that

|  |  |
| --- | --- |
|  |  |

And the unit projection operator is:

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |

So

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| --- | --- |
|  |  |

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| --- | --- |
|  |  |

Projecting G onto the r-basis:

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |

Bleah, this is going wack.

|  |  |
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|  |  |

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|  |  |

The expansion in spherical waves of the dimensionless outgoing free propagator:

|  |  |
| --- | --- |
|  |  |

About the fixed sites R and Rprime:

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |

Rehr and Albers define the propagator matrix elements as (Ref. Lloyd and Smith, Adv. Phys. 21, 69 (1972)):

|  |  |
| --- | --- |
|  |  |

The primary focus of RA’s paper is to define a form of the propagator which separates contributions from L and Lprime:

|  |  |
| --- | --- |
|  |  |
|  |  |

|  |  |
| --- | --- |
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| --- | --- |
|  |  |

# Multiple Scattering Theory

## The Dyson Equation

|  |  |
| --- | --- |
|  |  |

For the free atom:

|  |  |
| --- | --- |
|  |  |

Operating on both sides with the inverse operator:

|  |  |
| --- | --- |
|  |  |

Gives (multiplying through the minus sign):

|  |  |
| --- | --- |
|  |  |

The complete solution of equation 160 is the particular plus the general solution:

|  |  |
| --- | --- |
|  |  |

We know that this is the solution to the free atom case:

|  |  |
| --- | --- |
|  |  |

If we define the free space Green’s operator

|  |  |
| --- | --- |
|  |  |

Then

|  |  |
| --- | --- |
|  |  |

And in the multiple-scattering path formulation,

|  |  |
| --- | --- |
|  |  |

Now in the cluster scattering case,

|  |  |
| --- | --- |
|  |  |

Let’s define the symbol

|  |  |
| --- | --- |
|  |  |

So that

|  |  |
| --- | --- |
|  |  |

Expanding out,

|  |  |
| --- | --- |
|  |  |

Grouping terms,

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |

Define the full potential symbol

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |

Projecting this onto a set of phase shifted spherical waves at the absorber,

|  |  |
| --- | --- |
|  |  |

In the absence of the absorber potential, the wave function can be expanded in terms of free spherical waves. Outside of the muffin-tin sphere, the wave function can be expanded in terms of phase-shifted free spherical waves:

Returning to the MS derivation:

Projecting this onto a set of phase shifted spherical waves at the absorber, the coefficients of the expansion in free spherical waves about the absorber are:

|  |  |
| --- | --- |
|  |  |

Definition of T-matrices:

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |

So that

|  |  |
| --- | --- |
|  |  |

Expanding out,

|  |  |
| --- | --- |
|  |  |

Decomposition in spherical waves:

1. Expand field in the absence of the absorber potential in free spherical waves (analogous to derivation of Rayleigh relation when field is a plane wave)
2. Compare that to

|  |  |
| --- | --- |
|  |  |

To compute the amplitudes beta\_l.

So the coefficients

|  |  |
| --- | --- |
|  |  |

Where the alpha\_l are the coefficients of the expansion:

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |

Which in coordinate space is:

|  |  |
| --- | --- |
|  |  |
|  |  |

Comparing to the free wave:

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |

That’s an important expression, because the atomic wave function is

|  |  |
| --- | --- |
|  |  |

And the radial charge density is

|  |  |
| --- | --- |
|  |  |
|  |  |

Integrating this charge density over the muffin-tin gives:

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |
|  |  |

This last equation gives the total charge within the muffin-tin.

Alright, so the problem reduces to finding the betas:

|  |  |
| --- | --- |
|  |  |

For both the direct and full-scattering cases, the direct case being:

|  |  |
| --- | --- |
|  |  |

Define the coefficients for direct and full scattering as:

|  |  |
| --- | --- |
|  |  |
|  |  |

The chi-function represents the oscillatory part of the signal with respect to *angle of incidence*. In the expression for the total incident charge within the absorber muffin-tin, the only part that varies with angle is the beta:

|  |  |
| --- | --- |
|  |  |

HOWEVER, the muffin-tin integral WILL affect how each coefficient is weighted.

For right now, we’ll calculate the betas. THEN we’ll worry about how to handle the core wavefunctions.

One strategy – knowing the amplitudes beta of the free spherical waves, we can match the wave functions at the muffin-tin radius to determine the amplitude of the core wave function. But isn’t this what I tried to do before?

|  |  |
| --- | --- |
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| --- | --- |
|  |  |

Should it be?

|  |  |
| --- | --- |
|  |  |

And

|  |  |
| --- | --- |
|  |  |

Is the scattering t-matrix for the atom located at **R**, where

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |

## Direct term

Make note that we are assuming that the absorber is at the origin.

|  |  |
| --- | --- |
|  |  |
|  |  |

We replace the plane wave with its expansion in spherical waves (Rayleigh’s theorem):

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |

Since

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|  |  |

And that is the direct term.

Actually, one should note that the betas are a function of L and not just angular momentum.

The integrated charge is:

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |
|  |  |

Using Unsold’s Theorem:

|  |  |
| --- | --- |
|  |  |

Gives

|  |  |
| --- | --- |
|  |  |

And the magnetic quantum number does not matter here (as expected).

## Direct Term Not at Origin

|  |  |
| --- | --- |
|  |  |
|  |  |

Change variables:

|  |  |
| --- | --- |
|  |  |

|  |  |
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|  |  |

We replace the plane wave with its expansion in spherical waves (Rayleigh’s theorem):

|  |  |
| --- | --- |
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## Single-scattering term

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This result matches my earlier (1998) derivation when L = 0, except for a factor of 1 / (4 pi k) that comes from the redefinition of normalization in this work.

Normalization of GLL: If rho = 0 , I expect GLL = 1, check this.

|  |  |
| --- | --- |
|  |  |

The coefficients are:

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |

Where f is NOT a function of L.

The integrated charge is:

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |

Which, I’m thinking, is likely NOT independent of m. Then again, it could be. Better to just be explicit about it to be sure.

## Double-scattering term

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |

Inserting more complete sets, progressing from right to left,

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |

We define the scattering matrix:

|  |  |
| --- | --- |
|  |  |

And substituting:

|  |  |
| --- | --- |
|  |  |

We define the introduction matrix:

|  |  |
| --- | --- |
|  |  |

And substituting, we achieve the final result:

|  |  |
| --- | --- |
|  |  |

## Higher orders of scattering

Are achieved by inserting successive factors of the scattering matrix and corresponding spherical wave factors:

|  |  |
| --- | --- |
|  |  |

Summarizing:

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| --- | --- |
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|  |  |

Extension Method:

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| --- | --- |
|  |  |
|  |  |
|  |  |

Try redefining:

|  |  |
| --- | --- |
|  |  |
|  |  |

So that:

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| --- | --- |
|  |  |
|  |  |
|  |  |
|  |  |

The only place that khat appears is in the Q, so by calculating the series up to Q, we can quickly regenerate for different incident angles (i.e., by working with the RootAmplitude of all paths).

In matrix multiplication format, and for a single path and L:

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |

! Need to answer the question – for L = (l, m), do the n-values contribute or are they all the same for each m, meaning that the overall sum gains a factor of (2l + 1) and reduces to l-sum?

Try redefining:

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |

NOTE – need to modify the exponential in 390 to account for the inner potential decay.

HMM – SEE RA 1990 eq 23 and thereafter – an explanation for the factor of (-1)^m?

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |

Where the index n is the RA Order (typically 1, 3, or 6), and m is all (l,m) values, dimension:

|  |  |
| --- | --- |
|  |  |

So for Lmax = 10, m = 120.

With these definitions of the matrices, the amplitudes are calculated to be a column vector (rows in (l,m) and 1 column).

|  |  |
| --- | --- |
|  |  |

In explicit terms of **R**,

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |

Looking more closely at Q, it would be advantageous to separate out the terms that depend on khat:

|  |  |
| --- | --- |
|  |  |
|  |  |

Where

|  |  |
| --- | --- |
|  |  |
|  |  |

In matrix multiplication format, and for a single path and L:

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |

Exercise – we really need to calculate the time-reversed case for comparison, to validate that the above derivation is correct. Take a pure outgoing wave of angular momentum L and send it outwards. Treat the last scatterer as F-matrix with magnitude rho = infinity.

## Free Atom (Direct Term)

Calculate amplitude for each of the orbitals in the case of an incident plane wave and a single target atom.

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |

To within a normalization constant.

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |

## Outgoing Partial Wave Method

|  |  |
| --- | --- |
|  |  |

We assume that the outgoing wave function is composed of pure phase-shifted spherical waves.

|  |  |
| --- | --- |
|  |  |

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| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |

The first (direct) term:

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |
|  |  |

Expand the plane wave in terms of spherical harmonics:

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |

Total amplitude summing over all L:

|  |  |
| --- | --- |
|  |  |

Now that is the *direct* term.

Expanding the spherical harmonic in terms of the associated Legendre polynomial:

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |

I can see no obvious simplification here, although I’m sure there must be one (spherical symmetry due to sum over m).

|  |  |
| --- | --- |
|  |  |

Specific values for angular momenta:

|  |  |
| --- | --- |
|  |  |
|  |  |

## Multiple-Scattering Terms:

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| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |

I believe I need another free-space propagator in there, since the “first” scatterer is the absorber atom (already considered in the phase shift of the outgoing wave)

|  |  |
| --- | --- |
|  |  |

Single-scattering:

|  |  |
| --- | --- |
|  |  |

Here the sum over neighbors excludes the source atom.

|  |  |
| --- | --- |
|  |  |

Now, the wave function outside of the muffin tin is given by:

|  |  |
| --- | --- |
|  |  |

And the radial part of the wave function is:

|  |  |
| --- | --- |
|  |  |

With derivative w.r.t. r:

|  |  |
| --- | --- |
|  |  |

Now at the muffin-tin matching radius R, the logarithmic derivative must match:

|  |  |
| --- | --- |
|  |  |

Hmmm. That doesn’t work out right.

## Multiple Scattering Derivation

We wish to find the complete time-independent solution to the Schrodinger equation for the initial state of an electron incoming to an atom which is part of a solid:

|  |  |
| --- | --- |
|  |  |

Or

|  |  |
| --- | --- |
|  |  |

Where the full Hamiltonian is

|  |  |
| --- | --- |
|  |  |

Where it is understood that *H*0 is the free-space kinetic energy operator, *Va* is the potential of the atom which is to interact with the incident electron and the potentials *Vn* are those of the remaining atoms in the solid. The energy *E* is understood to be complex, containing a real, propagating part and a complex attenuating part.

|  |  |
| --- | --- |
|  |  |

## Free-space particular solution

The particular solution of Equation 160 is

|  |  |
| --- | --- |
|  |  |

Which has plane wave solutions

|  |  |
| --- | --- |
|  |  |

And wave number

|  |  |
| --- | --- |
|  |  |

In Hartree units

|  |  |
| --- | --- |
|  |  |

The general solution is

|  |  |
| --- | --- |
|  |  |

Operating on both sides with the inverse operator:

|  |  |
| --- | --- |
|  |  |

Gives (multiplying through the minus sign):

|  |  |
| --- | --- |
|  |  |

The complete solution of equation 160 is the particular plus the general solution:

|  |  |
| --- | --- |
|  |  |

If we define the free space Green’s operator

|  |  |
| --- | --- |
|  |  |

Then

|  |  |
| --- | --- |
|  |  |

## Atomic scattering particular solution

The particular solution of Equation 160 is

|  |  |
| --- | --- |
|  |  |

Which has solution, expanded in spherical harmonics:

|  |  |
| --- | --- |
|  |  |

The radial part of the solution is, in the region outside of the muffin-tin,

|  |  |
| --- | --- |
|  |  |

Inside of the muffin-tin, the wave function is the numerical solution.

The normalization constants a are chosen so that

|  |  |
| --- | --- |
|  |  |

Substituting:

|  |  |
| --- | --- |
|  |  |

The radial wave functions are infinite in extent, so we invoke volume normalization (the radial wave function is normalized such that):

|  |  |
| --- | --- |
|  |  |

Reduction of magnetic quantum number:

|  |  |
| --- | --- |
|  |  |

Since the integral over the radial wave functions is independent of m, each term contributes (2l+1) times:

|  |  |
| --- | --- |
|  |  |

Applying the definition of the normalization of the r-multiplied wave functions:

|  |  |
| --- | --- |
|  |  |

Applying the Basel problem, where

|  |  |
| --- | --- |
|  |  |

And then applying the principle of detailed balance, it must be true that

|  |  |
| --- | --- |
|  |  |

And therefore

|  |  |
| --- | --- |
|  |  |

This expression has been verified in Excel, and shows that the amplitude is dominated by the first few terms.

The general solution is

|  |  |
| --- | --- |
|  |  |

Operating on both sides with the inverse operator:

|  |  |
| --- | --- |
|  |  |

Gives (multiplying through the minus sign):

|  |  |
| --- | --- |
|  |  |

The complete solution of equation 160 is the particular plus the general solution:

|  |  |
| --- | --- |
|  |  |

If we define the free space Green’s operator

|  |  |
| --- | --- |
|  |  |

Then

|  |  |
| --- | --- |
|  |  |

Following Pendry’s discussion of the amplitude of partial waves:

Outside the range of the absorber muffin-tin potential, the total wave function can be decomposed into its partial waves:

|  |  |
| --- | --- |
|  |  |

Since the potential is spherically symmetric, the radial wave function cannot depend on the z-component of angular momentum *m*. In the region just outside of the muffin-tin boundary, the radial wave function has the form:

|  |  |
| --- | --- |
|  |  |

This form has the equivalent representation <http://galileo.phys.virginia.edu/classes/752.mf1i.spring03/Scattering_II.htm>:

|  |  |
| --- | --- |
|  |  |

The minus sign comes from the *standard* convention for Bessel and Neumann functions.

NOTE – there is a minus sign difference between the standard and Messiah conventions for the spherical Neumann function and therefore the spherical Hankel function. Pendry uses standard convention so let’s stick with that.

Now in the no-scattering case (no potential), the phase shift is zero.

We can decompose this expression into scattered and unscattered components:

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |

Note that both of these are radial wave functions, and gain a spherical harmonic in the full solution.

To find how a plane wave scatters, we decompose the plane wave in terms of spherical waves centered on the muffin-tin:

|  |  |
| --- | --- |
|  |  |

Note that there is no potential effect in this expression, so therefore by comparison is:

|  |  |
| --- | --- |
|  |  |

And the amplitude of each (direct) partial wave is:

|  |  |
| --- | --- |
|  |  |

Since this normalization must hold in the presence of the potential, we can construct the scattered wave as:

|  |  |
| --- | --- |
|  |  |

Adding these together and putting in the angular solution (spherical harmonics), the full solution is:

|  |  |
| --- | --- |
|  |  |

Connection to atomic wave functions:

We can utilize the amplitudes of the individual partial waves:

|  |  |
| --- | --- |
|  |  |

Knowing the charge density inside of the muffin-tin for each of the partial waves, we make the assertion that the total excitation cross-section scales like the (summed) total charge density.

* Take whatever the field is and expand it in partial waves about the origin
* Gives amplitude of each partial wave
* Apply modulus (a star a) to scale charge inside muffin-tin
* Add up and normalize to the direct wave.

1. Demonstrate that we can solve the direct wave case
2. Determine MS formulation for scattered waves, test with direct wave.

|  |  |
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|  |  |

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At the muffin-tin matching radius, these forms are equal:

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| --- | --- |
|  |  |

By the principle of detailed balance,

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| --- | --- |
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|  |  |
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OK, so we expand the full result in terms of (free) spherical waves about the absorber, then use that to determine the amplitude of each partial wave.

Returning to our previously-scheduled solution:

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Expanding out to the multiple-scattering series:

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| --- | --- |
|  |  |

In coordinate representation,

|  |  |
| --- | --- |
|  |  |

Successive terms are identified with the direct (no scattering) amplitude, single scattering, double scattering, etc. We will use the notation as follows to describe each of these terms:

|  |  |
| --- | --- |
|  |  |

This result will be expanded in terms of free spherical waves about the origin (absorber) to determine the amplitudes of each partial wave. Let’s do that for the first term (direct wave)

## Direct term

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |

We replace the plane wave with its expansion in spherical waves (Rayleigh’s theorem):

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| --- | --- | --- |
|  | |  |
|  | |  |
|  | |  |
|  | |  |
|  |  | |

Comparing this to the unscattered wave from partial wave theory:

|  |  |
| --- | --- |
|  |  |

We obtain the amplitudes of the partial waves for the direct term:

|  |  |
| --- | --- |
|  |  |

## Single scattering

|  |  |
| --- | --- |
|  |  |
|  |  |

Here we are introducing the notation

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |
|  |  |

We introduce the notation

|  |  |
| --- | --- |
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|  |  |

I’m going to assert:

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |
|  |  |

In coordinate representation this is:

|  |  |
| --- | --- |
|  |  |

Comparing this to the unscattered wave from partial wave theory:

|  |  |
| --- | --- |
|  |  |

We obtain the amplitudes of the partial waves for the direct term:

|  |  |
| --- | --- |
|  |  |

Now, by Rehr and Albers,

|  |  |
| --- | --- |
|  |  |

So

|  |  |
| --- | --- |
|  |  |

I’m disturbed by this – the free-space propagator contains r as a vector – this complicates the comparison to the unscattered form, and makes the coefficients functions of r (vector) – since we don’t know where on the sphere we will match. Essentially what this is saying is that the field at the muffin-tin boundary is non-uniform. Need to impose spherical symmetry on what is essentially a non-spherical problem. Options to match to the spherically symmetric muffin-tin interior:

1. Average the incident field over the muffin-tin boundary (easy)
2. Treat the problem as non-spherical symmetry (hard)

|  |  |
| --- | --- |
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|  |  |

Strategy – expand in spherical harmonics and integrate.

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|  |  |

Now what makes me wonder is that Rehr doesn’t do this for his calculation of EXAFS, which should be subject to the same termination condition. How does he do it? Another thing I just thought of – averaging won’t work for the amplitude, since it is complex – need to average the amplitude squared… but that loses phase information! Something wrong here…

# Definitions

## Orthogonality of state bases

|  |  |
| --- | --- |
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## Coordinate Representations

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## Projection Operators

|  |  |
| --- | --- |
|  | 1. P |

|  |  |
| --- | --- |
|  | 1. P |

|  |  |
| --- | --- |
|  |  |

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| --- | --- |
|  |  |

# Useful Identities

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| --- | --- |
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|  |  |
|  |  |

## Properties of spherical harmonics:

|  |  |
| --- | --- |
|  | 1. D |

|  |  |
| --- | --- |
|  | 1. P |

|  |  |
| --- | --- |
|  | 1. P |

## Properties of spherical Bessel functions:

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Note that the spherical Bessel functions are real-valued for real arguments.

## Properties of delta functions:

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| --- | --- |
|  |  |

Properties of plane waves

|  |  |
| --- | --- |
|  | 1. D |

(Rayleigh expansion)

|  |  |
| --- | --- |
|  | 1. ? |

(Unsöld’s theorem)

|  |  |
| --- | --- |
|  | 1. ? |

# Proofs

## Projection of plane wave in spherical wave basis:

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
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|  |  |

Expanding the plane wave in spherical harmonics:

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| --- | --- |
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## Projection of plane wave in offset spherical wave basis:

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| --- | --- |
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| --- | --- |
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|  |  |

Change variables:

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| --- | --- |
|  |  |

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| --- | --- |
|  |  |
|  |  |

Expanding the plane wave in spherical harmonics:

|  |  |
| --- | --- |
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|  |  |

## Proof of Rayleigh Formula:

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| --- | --- |
|  |  |

We begin with the plane wave projected onto the spherical wave basis:

|  |  |
| --- | --- |
|  |  |

We insert a complete set of states in the spherical wave basis:

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |

Since this is equal to

|  |  |
| --- | --- |
|  |  |
|  |  |

## Completeness of spherical wave basis

Assert that

|  |  |
| --- | --- |
|  |  |

Since we know

|  |  |
| --- | --- |
|  |  |

Inserting the complete set:

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |
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|  |  |
|  |  |
|  |  |

And the identity is proven.

## Unitariness of spherical wave projection operator:

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| --- | --- |
|  |  |

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|  |  |
|  |  |
|  |  |

## Normalization of the plane waves

In order for the k-space basis vectors to be orthogonal:

|  |  |
| --- | --- |
|  |  |

We insert the complete set:

|  |  |
| --- | --- |
|  |  |
|  |  |

Applying the expansion of the plane waves in spherical waves:

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| --- | --- |
|  |  |
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So the proper normalization of the plane waves in order to preserve this relation is:

|  |  |
| --- | --- |
|  |  |

## Orthonormality of spherical harmonics

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |

Since the Kronecker delta function is defined as:

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |
|  |  |

And by the properties of the associated Legendre polynomials:

|  |  |
| --- | --- |
|  |  |

Therefore

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |

And therefore the identity:

|  |  |
| --- | --- |
|  |  |

Is proven.

## Unitariness of the plane wave basis:

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |
|  |  |
|  |  |
|  |  |

## 

## Completeness of the k-space projection operator

Postulate:

|  |  |
| --- | --- |
|  |  |

Since we know that

|  |  |
| --- | --- |
|  |  |

Insert the postulated projection operator:

|  |  |
| --- | --- |
|  |  |

|  |  |
| --- | --- |
|  |  |

Expanding the exponentials in spherical harmonics:

|  |  |
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And therefore the identity is proven.

Spherical harmonic rotation matrices (from Messiah):

Where .

Half-angle formulas:

*t* runs over the set of values for which the factorials are ≥ 0.

Taking the natural log of the factorials,

The terms not involving *t* can be moved outside of the sum:

Where

Symmetry properties:

Special cases:

Tabulating some r’s:

For ℓ=2;

## Spherical Harmonics

In Rehr and Albers (PRB 41, 8139 (1990)) the spherical harmonics are defined as:

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Where

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Taken together, then, RA is using Laplace normalized spherical harmonics with the Condon-Shortley phase convention.

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For m < 0,

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And since

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Giving, finally,

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This is really just re-deriving the identity

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Rehr notes that since he specializes such that , for m < 0 he can effectively just drop the factor of and replace everywhere.

Now this means that in RA, the Legendre polynomials should *omit* the Condon-Shortley phase, so that instead of the normal definition

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Where the are the ordinary Legendre polynomials, we should use

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Also, we must be aware that Rehr and Albers use Hartree units and NOT Rydberg units.

Big question is, then, is Messiah using the same convention in his rotation matrices?

# Phase Shifted Spherical Wave Basis

In the absence of the absorber potential, the wave function can be expanded in terms of free spherical waves. Outside of the muffin-tin sphere, the wave function can be expanded in terms of phase-shifted free spherical waves:

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Properties of this basis:

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Proofs:

Since we know

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Inserting the complete set:

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And the identity is proven.

Orthogonality of the basis:

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Insert a complete set of states in coordinate space:

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And the orthogonality is proven.

Relationship to free spherical waves (non-shifted)

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To compute the amplitudes beta\_l.

So the coefficients

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Where the alpha\_l are the coefficients of the expansion:

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Which in coordinate space is:

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Comparing to the free wave:

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That’s an important expression, because the atomic wave function is

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## Direct Term Not at Origin – phase shifted basis

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Change variables:

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We replace the plane wave with its expansion in spherical waves (Rayleigh’s theorem):

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## Direct Term at Origin – No Absorber

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## Direct Term Not at Origin – No Absorber

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## Single-scattering term – no absorber

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# Hand calculation – Two Si atoms

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Atom 0 at position (0,0,0)

Atom 1 at position (1,0,2)

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For E = 30 eV and V0 = -16 eV, Etotal = 46 eV and k = 3.474

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Now since I’m only taking the L = (0,0) component, the gammatwiddle term restricts lamda to be 0,0 as well (all others are zero).

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Since

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In Cartesian coordinates. The same in spherical coordinates is:

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Theta = 2.678, phi = 0.

Introducing some hard numbers,

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Define

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We’ll define this as the function

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Now let’s dive into the sum over angular momentum. Define

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Now khat is

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In Cartesian coordinates. The same in spherical coordinates is:

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And for rhohat, Theta = 2.678, phi = 0.

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Since

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Pulling it all together,

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And the real intensity is:

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Let’s step back a bit first and make some definitions to help this along:

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Define

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So that

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Now computing the real intensity is a bit simpler:

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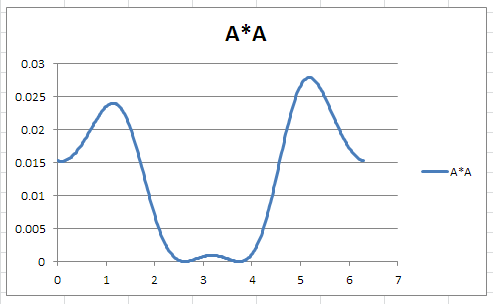
Break it down term by term:

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Bleah bleah bleah. This is way too long and hard.

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Ugh. This doesn’t match either of them, and looks asymmetric to boot.

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In spherical coordinates,

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NOTE – we’re using unrefracted Theta.

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So,

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Now

T0 = -0.461950643930397 + 0.691315453041022i

T1 = -0.122379071762125 + 0.0152079179744779i

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Now add t0:

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What remains now is to calculate 1/rho times the exponential.

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Putting it together,

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In the DESD code, the direct amplitude is:

0.08118799125561 + 0i

Compare to

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Which is correct.

So the issue must be in the single scattering part.

It’s almost like things aren’t interfering…

Checking phi =0 amplitudes:

0, 0.08118799125561 + 0i

0-1, -0.00938398432480866 + 0.000878307339411526i

Summing,

A = 0.8025 + 0.000878 i

Looks like the A\*A is going correctly.

NOTE – the hand calculation is slightly off the Mathcad and (fixed) DESD calculations, due to roundoff error.

