# Queen Mary, University of London

## School of Physics and Astronomy

# Scattering Theory and XAFS Calculation

Conduction Band

Gap

Valence Band
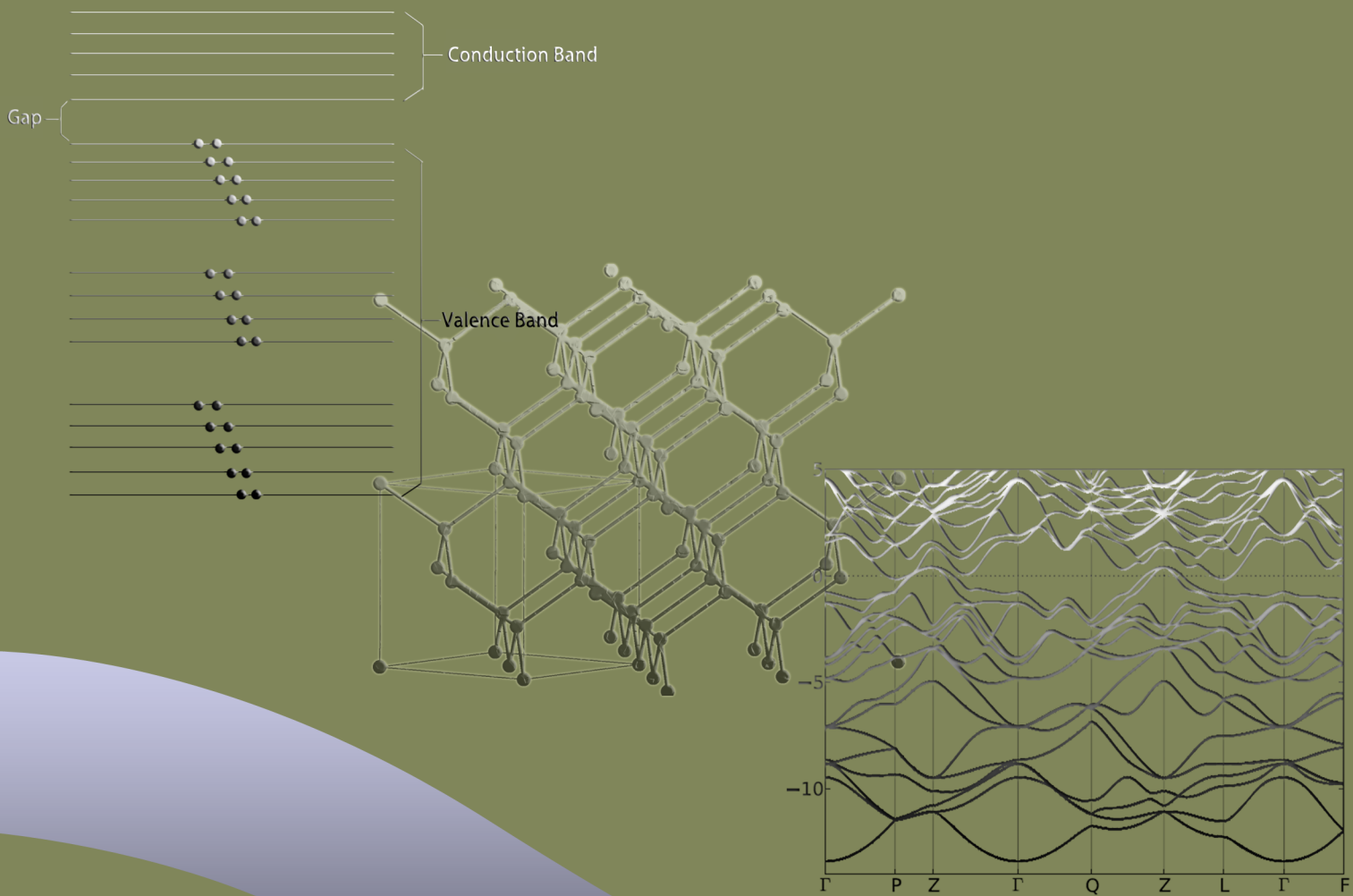
## 1. Multiple-Scattering Expansion in Scattering Theory

When we are talking about the scattering, naturally we should have what is scattered — the incoming wave, and also what the result is of the scattering — scattered wave. For the incoming wave, typically it is taken as the free wave since we are talking about the wave coming from infinitely far away from the 'scatterer', where the potential is set to be 0. Therefore, the Schrödinger equation for the incoming wave is simply as:

$$(E - H_0)|\psi_0\rangle = 0 \tag{1-1}$$

where the Hamiltonian $H_0$ is the *background Hamiltonian*:

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 \tag{1-2}$$

When we focus on the interaction between the incoming wave and the 'scatterer', we are actually talking about the effect of scattering potential $V(r)$ on the incoming wave. And the goal of scattering theory is just to solve the energy eigenvalue (we will talk about the energy eigenvalue later) for the perturbed occasion. The corresponding Schrödinger equation then becomes:

$$[E - H_0]|\psi\rangle = V|\psi\rangle \tag{1-3}$$

Since we are talking about scattering, which means the 'net' scattering effect excluding the incoming wave. However in equation - (1-3), the wavefunction $|\psi\rangle$ indeed contains the contribution from the incoming wave. Hence the basic idea is to define a 'pure' scattered wavefunction $|\psi_s\rangle$ as following:

$$|\psi_s\rangle = |\psi\rangle - |\psi_0\rangle \tag{1-4}$$

Then we should have:

$$(E - H_0)(|\psi_s\rangle + |\psi_0\rangle) = V|\psi\rangle \tag{1-5}$$

by substituting (1-4) to (1-3). Then by using equation - (1-1) we should have:

$$(E - H_0)|\psi_s\rangle = V|\psi\rangle \tag{1-6}$$

Here there is a problem about the eigenvalue. Considering (1-1) and (1-3), is the energy $E$ in each equation naturally the same? No! In (1-1), 'E' is actually for free wave (plane wave). However for (1-3) when we have the potential, the 'E' is no longer for free wave but for final scattered wave, i.e. the 'E' in this case corresponds to $|\psi\rangle$ but not $|\psi_0\rangle$. That means we cannot go directly from (1-5) to (1-6) by using (1-1) since the 'E' in (1-1) and (1-3) is different! But why we still have (1-6)? Is there anything wrong? No, that's because we regard the energy eigenvalue for the incoming and final outgoing wave as the same. Why? Because we are talking about the scattering problem using the time-independent perturbation theory, in which we regard the potential as perturbation to the initial state (incoming wave) and more importantly we are not focusing on the change of energy eigenvalue. Thus we assume the energy is kept the same before and after the scattering, and that's definitely true for elastic problem (for inelastic scattering, corresponding correction should then be added, which is beyond the scope of this article)!

Then we could easily write down the solution for equation - (1-6) as:

$$|\psi_s\rangle = (E - H_0)^{-1}V|\psi\rangle \tag{1-7}$$

Here it should be pointed out that the operator $(E - H_0)^{-1}$ is only an abstract inverse operation of $(E - H_0)$. Moreover, this is indeed the idea of Green's function. If we write down the equation - (1-7) again, however in real space, we should have:

$$(E + \frac{\hbar^2}{2m}\nabla^2)\psi_s(r) = V(r)\psi(r) \tag{1-8}$$

Then for equation - (1-8), we could say that if we find its corresponding Green's function $G(r, r^{'})$, we have got the solution as following:

$$\psi_s(r) = \int G(r, r^{'})V(r^{'})\psi(r^{'})dr^{'} \tag{1-9}$$

By comparing (1-9) with (1-7), we can find that they are basically the same. Then by adding $|\phi_0\rangle$ on both sides of (1-7), we could have:

$$|\phi_\rangle = |\phi_0\rangle + (E - H_0)^{-1}V|\phi\rangle \tag{1-10}$$

Hereby we can say that we have already separate the influence from the free propagator and the scattering effect by writing the final wavefunction as the sum form as (1-10). And (1-10) is called Lippman-Schwinger equation.

As is already said above, the function of operator $(E - H_0)^{-1}$ is indeed the same with that of Green's function in this case, hence we compactly write down $(E - H_0)^{-1}$ as the Green's operator $G_0 = (E - H_0)^{-1}$ (actually, the exact form of Green's operator should also contain corresponding complex component in the denominator, here for simplicity we ignore the complex form for now). Then (1-10) becomes:

$$|\phi_\rangle = |\phi_0\rangle + G_0V|\phi\rangle \tag{1-11}$$

Formally, solving equation - (1-11) is quite simple by rearranging (1-11) to give:

$$|\psi\rangle = (1 - G_0V)^{-1}|\psi_0\rangle \tag{1-12}$$

However, later in the next section we will see that writing the solution for final wavefunction in scattering problem in the way like (1-12) is actually kind of 'direct' way to solve the corresponding Schr$\ddot{o}$ dinger equation. Here recalling our basic idea of separating the final wavefunction to free propagator part (which is indeed the incoming wave) and the 'pure' scattered part, we then look at (1-12) from another viewpoint to give:

$$|\psi_{new}\rangle = |\psi_0\rangle + G_0V|\psi_{old}\rangle \tag{1-13}$$

in which $|\psi_{old}\rangle$ means our 'old' guess for the solution of final wavefunction, and $|\psi_{new}\rangle$ is our new final wavefunction based on the previous guess. Thereby keeping writing the solution for final wavefunction iteratively in the way given by (1-13), finally we should have:

$$|\psi\rangle = (1 + G_0V + G_0VG_0V + G_0VG_0VG_0V + \cdots)\psi_0\rangle \tag{1-14}$$

Then for the right side of (1-14), the first term within the bracket refers to the free propagator and all the other terms concern about the scattering following all possible paths. Therefore we see that by using the method given by (1-13), we successfully write down the solution for final wavefunction as the sum of free propagator and the 'pure' scattering path. And more importantly, the solution form of (1-14) is just the so-called multiple scattering expansion, which is easy to understand and compute. Since this material is the basic introduction of Green's function method in scattering problem, we are not going into details about the real calculation for Green's operator and also the final wavefunction. For detailed information, refer to Introduction to Scattering Theory. Considering our previous definition for $|\psi_s\rangle = |\psi\rangle - |\psi_0\rangle$, we could write down (1-14) in another way:

$$|\psi_s\rangle = G_0(V + VG_0V + VG_0VG_0V + \cdots)\psi_0\rangle \tag{1-15}$$

which then gives the 'pure' scattering wavefunction $|\psi_s\rangle$. Furthermore, if write all of the scattering story into a compact 'black box':

$$T = V + VG_0V + VG_0VG_0V + \cdots \qquad (1\text{-}16)$$

Here we write down (1-7) and (1-12) together:

$$|\psi_s\rangle = G_0V|\psi\rangle \qquad (1\text{-}17)$$
$$|\psi\rangle = (1 - G_0V)^{-1}|\psi_0\rangle \qquad (1\text{-}18)$$

Taking into account of (1-16) - (1-18), we could then obtain:

$$T = (1 - VG_0)^{-1}V \qquad (1\text{-}19)$$

Here the operator $T$ is called T-matrix, which takes all scattering related effects into account.

Before we end up this section, there are still two main points which should be addressed briefly. Firstly, the multiple scattering expansion series given in (1-14) is called the *Bornseries*; however, the *Bornseries* could possibly not convergent, which makes it quite difficult to calculate final state wavefunction (excited state but not ground state) within the framework of multiple scattering. Of course the convergent problem also exist for (1-15) and (1-16). In the online material Introduction to Scattering Theory, the convergent problem is discussed in details. Secondly, also in the above online material, there is given the relationship between the scattering amplitude and T-matrix as following:

$$f(\vec{k}', \vec{k}) = -\frac{(2\pi)^2 m}{\hbar^2}\langle\vec{k}'|T|\vec{k}\rangle \qquad (1\text{-}20)$$

which should be interpreted as the probability amplitude of scattering in the direction $\vec{k}'$, given an incident wave vector $\vec{k}$. As for how we extract the scattering amplitude $f(\vec{k}', \vec{k})$, it will not be discussed in this article (refer to the above online material). However it should be pointed out that T-matrix describes the scattering field over the whole space, therefore correspondingly $f(\vec{k}', \vec{k})$ in this case actually is the scattering amplitude described in k-space (momentum space).

## 2.    KKR Method

Again we go back to the basic Schrödinger equation in scattering potential field as given by (1-3), and here we write it down directly without using Dirac symbols:

$$[\frac{\hbar^2}{2m}\nabla^2 + E(\mathbf{k})]\psi_{\mathbf{k}}(\mathbf{r}) = V(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r}) \qquad (2\text{-}1)$$

Here not like the discussion about energy eigenvalue in section - (1), we do not consider whether the energy of initial and the 'perturbed' state is different or not. Actually we can write down the solution form compactly using Green's function method to give:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \int_{\Omega_0} d^3r' G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}')V(\mathbf{r}')\psi_{\mathbf{k}(\mathbf{r}')} \qquad (2\text{-}2)$$

where we put all scattering related terms (the crystal structure, dependence on $\mathbf{k}$ - the energy changing between initial and final state) into Green's function $G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}')$. And the Green's function $G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}')$ in this case should satisfy:

$$[\frac{\hbar^2}{2m}\nabla^2 + E(\mathbf{k})]G_{\mathbf{k}(\mathbf{r}-\mathbf{r}')} = \delta(\mathbf{r} - \mathbf{r}') \qquad (2\text{-}3)$$

The solution form given by (2-3) for Schrödinger equation in scattering potential field is quite neat and compact. However the tough question then becomes how we are going to obtain the Green's function $G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}')$. In the online material The Green's function method (KKR method), it is discussed in details how to obtain the Green's function to get the solution for final state wavefunction. Here in this article, we only give the brief summary of that online material, which only contains the basic idea but not specific calculation and deduction procedures.

Basically, what we going to do is to define a function $\bar{\Lambda}$, and use the variational principle to get the equation: $\delta\bar{\Lambda} = 0$. And we will find the solution for the equation $\delta\bar{\Lambda} = 0$ is exactly the same with (2-2). That we means we can obtain our final state wavefunction through solving the variational equation $\delta\bar{\Lambda} = 0$. Then the question becomes: How are we going to solve $\delta\bar{\Lambda} = 0$? Here we directly give the form for $\bar{\Lambda}$:

$$\bar{\Lambda} = \int_{\Omega_0} d^3\psi_{\mathbf{k}}^*(\mathbf{r})(\hat{H} - E)\psi_{\mathbf{k}}(\mathbf{r})$$

$$= \int_{\Omega_0} d^3r\psi_{\mathbf{k}}^*(\mathbf{r})V(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r}) - \int_{\Omega_0} d^3r\psi_{\mathbf{k}}^*(\mathbf{r})[\frac{\hbar^2}{2m} + E]\psi_{\mathbf{k}}(\mathbf{r}) \tag{2-4}$$

$$= \int_{\Omega_0} d^3r\psi_{\mathbf{k}}^*(\mathbf{r})V(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r}) - \int_{\Omega_0}\int_{\Omega_0'} d^3r d^3r' \psi_{\mathbf{k}}^*(\mathbf{r})V(\mathbf{r})G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}')V(\mathbf{r}')\psi_{\mathbf{k}}(\mathbf{r}') \tag{2-5}$$

Therefore basically, when we use the variational principle on equation -(2-5), we will definitely get the solution which is just that given by (2-2).

Then there comes an important approximation to help us solving the variational equation $\bar{\Lambda} = 0$ — the Muffin-Tin approximation for the potential:

$$V(\mathbf{r}) = \begin{cases} V(|\mathbf{r}|) & r \leq r_{MT} \\ 0 & r > r_{MT} \end{cases} \tag{2-6}$$

Then the integration in (2-5) is only non-zero within the area where $r \leq r_{MT}$. More importantly, within this area we can write down our solution for the final state wavefunction $\psi_{\mathbf{k}}(\mathbf{r})$ as the linear combination of some basis wavefunctions. What are those basis functions then? Since the potential given by (2-6) is spherically symmetric, if recalling the separate variables method to deal with the spherically symmetric potential field, we probably get a rough idea about what is going to happen. When we have spherically symmetric potential, we write down the Schrödinger equation in spherical coordinate and separate our equation into two independent equations (radial part and angular part) by writing our solution following:

$$\psi_{\mathbf{k}}^{SS}(\mathbf{r}) = R(r)Y(\theta, \phi) \tag{2-7}$$

By solving the separate Schrödinger equation we could obtain our final solution for wavefunction with the form given by (2-7). Based on the discussion above, we can now write down the guess solution form for our final state wavefunction following:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{l=0}^{\infty}\sum_{m=-l}^{m=+l} c_{lm}(\mathbf{k})\phi_{lm}(\mathbf{r}; E) = \sum_{l=0}^{\infty}\sum_{m=-l}^{m=+l} c_{lm}R_l(r; E)Y_{lm}(\theta, \phi) \tag{2-8}$$

Therefore, the only unknowns for our final state wavefunction becomes the linear coefficients $c_{lm}$. Then recalling our variational principle $\delta\Lambda = 0$, so by inserting our guess solution (2-8) into (2-5) and applying the variational principle, we could in principle obtain the equations which only contain

the coefficient unknowns $c_{lm}$. Here we directly give the equations that $c_{lm}$ satisfies, which is actually homogeneous linear equations thus can be written in a compact form as following:

$$\sum_{l'm'} \Lambda_{lm,l'm'}(\mathbf{k})c_{l'm'}(\mathbf{k}) = 0 \tag{2-9}$$

In this case, all of our tedious integrations go into $\Lambda_{lm,l'm'}(\mathbf{k})$ which is given by:

$$\Lambda_{lm,l'm'}(\mathbf{k}) = \int_{MTK} d^3 r \phi_{lm}^*(\mathbf{r}; E) V(r) \phi_{l'm'}(\mathbf{r}; E) -$$
$$\int_{MTK} \int_{MTK'} d^3 r d^3 r' \phi_{lm}^*(\mathbf{r}; E) V(r) G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') V(r') \phi_{l'm'}(\mathbf{r}'; E) \tag{2-10}$$

Here before continuing, it should be pointed out that the homogeneous linear equations (2-9) can be written in matrix form and out matrix elements are just $\Lambda_{lm,l'm'}(\mathbf{k})$ where $(l,m)$ together labels the row and $(l',m')$ together labels our column. And remember our integration area changes based on the muffin-tin potential approximation, which is represented with $MTK$ in equation - (2-10).

In principle, we have finished our task here holding the equation - (2-9) in hand while keeping in mind the matrix element of $\Lambda_{lm,l'm'}(\mathbf{k})$ given by (2-10). To better understand this point here, it is better to write down the equation - (2-9) again in matrix form:

$$M_{\Lambda_{lm,l'm'}} C_{l'm'} = 0 \tag{2-11}$$

where $M_{\Lambda_{lm,l'm'}}$ is our matrix with elements $\Lambda_{lm,l'm'}$ and $C_{l'm'}$ is the column containing our coefficient unknowns $c_{l'm'}$. Technically, the equation - (2-11) is called secular equation. Then what is the prerequisite for equation - (2-11) to have non-zero solutions? From the linear algebra we know that the determinant of matrix $M_{\Lambda_{lm,l'm'}}$ should be 0, i.e.:

$$Det\{M_{\Lambda_{lm,l'm'}}\} = 0 \tag{2-12}$$

What does equation - (2-12) tell us? If we go back and have a look at our matrix element $\Lambda_{lm,l'm'}$ given by (2-10), we should notice that the only unknowns in there is the Green's function $G_{\mathbf{k}(\mathbf{r}-\mathbf{r}')}$. Then we have the equation - (2-12), therefore in principle we can obtain the Green's function $G_{\mathbf{k}(\mathbf{r}-\mathbf{r}')}$ by solving (2-12). In the online material The Green's function method (KKR method), it is discussed in details how to transform (2-12) to another form which is easy for us to solve it. Basically, each component in the matrix element ($\phi_{lm}(\mathbf{r}; E)$ and $G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}')$) is expanded or written in another way, and for details, refer to Page199-202 in the material following the link given above.

Compared to the multiple-scattering method expansion method given in section-1, here for KKR method based on variational principle we don't have the problem that whether the energy changes before and after the scattering process since we didn't even separate incoming wave from the final result by putting all stuff into Green's function $G_{\mathbf{k}(\mathbf{r}-\mathbf{r}')}$. Moreover, we also don't have the convergent problem as it is in multiple-scattering expansion framework. However is the method given in this particular section without any limitations? Yes, it indeed has its own limitation! Recalling our guess solution for $\psi_{\mathbf{k}(\mathbf{r})}$, there we have our expansion index $l$ and $m$ and also there we set the index $l$ to infinity. Is that possible? Of course not! Based on above discussion, we finally to deal with the matrix $M_{\Lambda_{lm,l'm'}}$. For computer, we should definitely have our upper limit for $l$ to go (the value of $m$ is determined automatically by $l$ with $m = -l, -l+1, \cdots, l-1, l$), and let's say our upper limit is set to be $l_{max}$. Then the matrix $M_{\Lambda_{lm,l'm'}}$ should be with the order of:

$$(l_{max} + 1)^2 \tag{2-13}$$

We could notice that the order of matrix $M_{\Lambda_{lm,l'm'}}$ increases rapidly as we increase our upper limit for $l$, and finally we could easily go beyond the computation capability of modern computers. This makes it difficult to deal with the high energy part of X-ray absorption spectra calculation (for relation between absorption and the final state wavefunction talked about here, refer to next section), since if we have high energy value we should need corresponding large angular momentum components (large $l_{max}$). That's where FEFF algorithm given by Rehr and Albers comes to help, which will be talked about in next section.

Before we end up with this section, it should be pointed out that in 1947, Korringa (the first 'K' in 'KKR') introduced general scattering theory into the secular equation (2-11), which then directly give the phase shift (about phase shift, refer to Scattering Theory Basics) during the scattering process.

## 3.    Scattering Theory In FEFF

The discussion in this section is mainly based on the paper by Rehr and Albers [1] and also Bruce Bunker's book about XAFS [2]. First of all, we should point out the relationship between X-ray absorption spectrum and what we are talking about in section (1) and (2) (the final state wavefunction and corresponding Green's function). According to the Fermi's Golden Rule, the absorption coefficient of X-ray is given by:

$$\mu = \frac{2\pi}{\hbar}|\langle\psi_f|H'|\psi_i\rangle|^2\rho \tag{3-1}$$

where $\psi_f$ and $\psi_i$ are respectively the initial and final states, of energy $E_f$ and $E_i$, $\rho$ is the density of states, and $H'$ is the interaction Hamiltonian between the electromagnetic field and the electrons. Given the form of interaction Hamiltonian as:

$$H' = \vec{A} \cdot \vec{p} \tag{3-2}$$

where $\vec{A}$ is the vector potential of the wave and $\vec{p}$ is the momentum operator of the electron, (3-1) transforms to:

$$\mu \propto |\langle\psi_f|\hat{\epsilon} \cdot \vec{r}e^{i\vec{k}\cdot\vec{r}}|\psi_i\rangle|^2\rho(E_f - E_i - \hbar\omega) \tag{3-3}$$

and $\hat{\epsilon}$, $\hbar\vec{k}$ and $\hbar\omega$ are the X-ray's electric polarization vector, momentum and energy. In the dipole approximation (for more about dipole approximation, refer to Quantum Transition in Chinese), (3-3) can be written as:

$$\mu(E) \propto \sum_f \langle i|\hat{\epsilon} \cdot \vec{r}'|f\rangle\delta(E - E_f)\langle f|\hat{\epsilon} \cdot \vec{r}|i\rangle \tag{3-4}$$

Here it should be pointed out that the absorption coefficient given by (3-4) includes all possible transition, which means we take into account of all possible final states. When we consider only one final state (imagine we are dealing with Ge K-edge absorption problem), then (3-4) actually becomes:

$$\mu(E) \propto |\langle i|\hat{\epsilon} \cdot \vec{r}|f\rangle|^2 \tag{3-5}$$

Moreover, if we define the Green's operator following:

$$(-1/\pi)Im\,G = \sum_f |f\rangle\delta(E - E_f)\langle f| \tag{3-6}$$

Then we can write down (3-4) in a compact form as:

$$\mu(E) \propto (-1/\pi)Im\langle i|\hat{\epsilon} \cdot \vec{r}'\,G\,\hat{\epsilon} \cdot \vec{r}|i\rangle \tag{3-7}$$

Here it seems that the defined Green's operator does give us something new, however is it really the case? Let's write down the specific form of Green's operator (for details, refer to Green's function):

$$G(\vec{r}, \vec{r}'; E) = \sum_n \frac{\psi_n(\vec{r}')\psi_n^*(\vec{r})}{E - E_n + i\eta} \tag{3-8}$$

we can find that when we put (3-8) back into the compact expression for absorption coefficient (3-7), the final expression is exactly the same with (3-4). There is nothing new here! Therefore it seems for now that the only reason we write down the absorption coefficient calculation expression in the form of (3-6) is that the form of Green's operator given by (3-9) (which corresponds to our final state wavefunction) does 'fit' into our Fermi's Golden rule in dipole approximation — equation - (3-4). And our task does not change at all — to find the solutions for final state — $\psi_n(\vec{r})$. If everything stops here, then there is indeed nothing new. But why do we bother with building up the Green's operator following (3-9)? Why don't we directly feed our obtained final states wavefunction into (3-4)? That's because the defined Green's operator does bring us something new, since it turns out that we have other ways to obtain the Green's operator but not following its definition form in (3-9)! How? The section (1) has already given us the option — through multiple-scattering expansion. However there is a problem for multiple-scattering expansion method. We already know that the wavefunction within the muffin-tin radius is spherical wave, then the outgoing wave should be definitely spherical wave, since the potential outside the muffin-tin radius is set to be 0. So the outgoing wave is not influenced in the interstitial region, which means the wave reaching next atom in the scattering path is still spherical, which makes it difficult to calculate the 'next' outgoing wave (recalling that the multiple-scattering expansion series is actually based on the assumption that the incoming wave is plane wave). Then how do we deal with the 'spherical' problem?

To solve this 'spherical' problem, the typical method is to 'manually' set the original outgoing spherical wave between interstitial area to plane wave, and this approximation is referred to as Plane Wave Approximation (PWA). Within the PWA framework, the multiple scattering path with N-legs (1 absorber and (N-1) scatterer) is given by [1]:

$$\chi^{(N-1)}(k) = Im\left[\frac{e^{i(\rho_1+\rho_2+\cdots+\rho_N)+2i\delta_1}}{\rho_1\rho_2\cdots\rho_N}(\hat{\rho}_1 \cdot \hat{\rho}_N)f_{N-1}(\theta_{N-1})\cdots f_2(\theta_2)f_1(\theta_1)\right] \tag{3-9}$$

where $k$ is the photoelectron wave number, $f_i(\theta_i)$ is the dimensionless plane-wave scattering amplitude at the $i$th scatter, $\boldsymbol{\rho}_i = k(\mathbf{R}_{i+1} - \mathbf{R}_i)$ is the dimensionless bond vector, and $\theta_i = cos^{-1}(\hat{\rho}_i \cdot \hat{\rho}_{i+1})$ is the scattering angle at site $i$. For amplitude $f(\theta)$, the usual definition form is given in $1-20$, and in partial wave frame, it is given by (refer to Scattering Theory Basics):

$$f(\theta) = \sum_l (2l+1)t_l P_l(cos\theta) \tag{3-10}$$

where $t_l = exp(i\delta_l)sin(\delta_l)$ is the dimensionless scattering $t$ matrix, and $P_l(cos\theta)$ is a Legendre polynomial of order $l$ (compared to the original form of $f$ as given in the above reference material, the $f$ here lacks the factor of $k$). As we already know, the PWA framework could easily fail to give correction description for near-edge absorption spectrum because of the convergent or some other problems (e.g. the curved-wave effects become increasingly important). And Rehr's paper [1] tries to go beyond the problem caused by PWA, which will be discussed later in this article. Before that, we should give the description for single and multiple-scattering as following: Fig. 1 (a) shows the single scattering path. Each single-scattering path is with 2 leges, and there is only absorption atom and the scatterer in the path. For multiple-scattering, the scattering wave may wonder around surrounding atoms
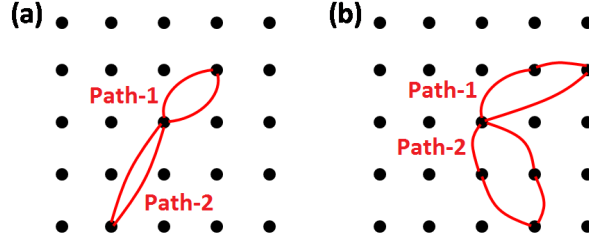
Figure. 1 The illustration for (a) - single and (b) - multiple-scattering.

(scatterer) and finally goes back to the absorption atom, as shown in Fig. 1 (b). The expression given by (3-9) is for multiple-scattering path with N legs, however if set N to 2, then it becomes single scattering. To beyond the PWA, in the case of single-scattering, we can define effective scattering amplitude that take spherical-wave effects into account exactly [1]. However, Rehr [1] believes that this approach is not quite suitable for multiple-scattering problem since we may introduce the 'accumulation problem'. Thus Rehr and Albers proposed keeping the multiple-scattering expansion form (3-9) not changed while replacing the plane-wave scattering amplitude with the corresponding scattering amplitude matrix to account for multiple-scattering problems. Here we directly give the final Green's function form derived by Rehr and Albers [1]:

$$G_{L_N,L_0}^{(N-1)}(\mathbf{R}_1,\cdots,\mathbf{R}_N) = \frac{e^{(\rho_1+\rho_2+\cdots+\rho_N)}}{\rho_1\rho_2\cdots\rho_N}\sum_{\{\lambda_i\}} M_{\lambda_1,\lambda_N}^{L_0,L_N}(\boldsymbol{\rho}_1,\boldsymbol{\rho}_N)F_{\lambda_N,\lambda_{N-1}}(\boldsymbol{\rho}_N,\boldsymbol{\rho}_{N-1})\times\cdots$$

$$\times\cdots\times F_{\lambda_3,\lambda_2}(\boldsymbol{\rho}_3,\boldsymbol{\rho}_2)F_{\lambda_2,\lambda_1}(\boldsymbol{\rho}_2,\boldsymbol{\rho}_1) \qquad (3\text{-}11)$$

where $F_{\lambda\lambda'}(\boldsymbol{\rho},\boldsymbol{\rho}')$ is just the scattering-amplitude matrix and $M_{\lambda_1,\lambda_N}^{L_0,L_N}(\boldsymbol{\rho}_1,\boldsymbol{\rho}_N)$ is the termination matrix. Then for path $\Gamma$, the multiple-scattering expansion $\chi_\Gamma(k)$ is given by [2]:

$$\chi_\Gamma(k) = ImS_0^2 \frac{e^{i(\rho_1+\rho_1+\cdots+\rho_N+2\delta_1)}}{\rho_1\rho_2\cdots\rho_N}e^{-\delta_\Gamma^2 k^2/2\hbar^2}\times Tr[MF^N\cdots F^2F^1] \qquad (3\text{-}12)$$

where $S_0^2$ is the passive amplitude factor that accounts for the overlap between the wavefunctions of the passive electrons in the initial and final states, $Tr$ represents the trace, and $\delta_\Gamma$ is the Debye-Waller factor for path $\Gamma$, accounting for the effect of disorder (including dynamic and static disorder). It should be pointed out that although the new multiple-scattering expansion expression (3-12) is similar to (3-9), it is actually a 'corrected' PWA version for multiple-scattering expansion by replacing the plane-wave scattering amplitude with the scattering-amplitude matrix.

Before the end of the whole section here, there are still several aspects to point out. The first thing is about the common EXAFS expression:

$$\chi(k) = \sum_j \frac{N_j e^{-2k^2\delta_j^2}e^{-2R_j/\lambda(k)}f_j(k)}{kR_j^2}sin[2kR_j+\delta_j(k)] \qquad (3\text{-}13)$$

which was first derived by Stern, Sayer and Lytle [2]. Actually, it should be noticed that expression (3-13) for EXAFS is based on single-scattering and plane-wave approximation, which is obviously not appropriate for XANES region where multiple-scattering effect becomes dominant. The second thing is that although FEFF algorithm proposed by Rehr and Albers works well for the whole XAFS spectrum calculation, the latest version of FEFF (FEFF9.6) does give us the option to deal with

the near-edge problem using full multiple-scattering (FMS) method, which is mainly introduced in section - (2). However for Artemis program (designed by Bruce Ravel, et al. [3] for EXAFS data fitting to extract structural information), embeds only the early version of FEFF (FEFF6) which does not give us the option to use FMS method.

## References

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