Multiple Scattering Theory in a General Basis *

ZHAO Hai-Feng[1;1)] WU Zi-Yu[1;2)] Sebilleau Didier[2;3)]

1 (Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, CAS, Beijing 100049, China)
2 (Equipe de Physique des Surfaces et des Interfaces, Laboratoire de Physique des Atomes, Lasers, Molécules et Surfaces, UMR CNRS-Université 6627, Université de Rennes 1, 35042 Rennes Cédex, France)

Abstract We present a theory to describe multiple scattering (MS) with an arbitrary basis. This framework allows us to select a set of new basis that exhibits better convergent properties than the usual spherical wave basis. Therefore, it enables us to perform faster and less memory-consuming calculations. Although the method outlined here is quite general, it gives a better description of the scattering properties and consequently reduces the size of the two block matrices involved in the MS calculation.

Key words multiple scattering theory, basis function, operator, computation

1 Introduction

In the last thirty years, multiple scattering (MS) theory has achieved a great success in understanding the physical structure and the chemical surrounding of systems in many scientific fields[1]. The base of the theory relies on the precise description of different scattering processes in which the electron (or any other particle) penetrates and propagates into a material composed by numerous atoms. Many properties of the investigated system can be modeled by this theory, for instance the electronic structure, and many standard spectroscopies which can be used to extract the information from the materials can easily be described by the MS theory[2].

The whole MS theory can be formulated in terms of the scattering path operator[3] $\tau^{ji}_{L_jL_i}$ which describes all the possibilities of the wave function starting from the i-th atom with angular momentum $L_i \equiv (l_i, m_i)$ and ending at the j-th atom with angular momentum L_j. Technically speaking, the scattering path operator $\tau^{ji}_{L_jL_i}$, which connects i-th and j-th atoms, can be written in the form of

$$\tau^{ji}_{L_jL_i} = [(T^{-1}+G)^{-1}]^{ji}_{L_jL_i} \ , \qquad (1)$$

where T is the transition matrix, e.g. the T-matrix, satisfying $[T]^{ji}_{L_jL_i} = -2\dfrac{k}{\pi}t_{l_j}\delta_{ji}\delta_{L_jL_i}$, δ_{l_j} denotes the phase shift of the j-th atom scattered by the potential, the scattering amplitude t_{l_j} is given by $t_{l_j} = \sin\delta_{l_j}\exp(\mathrm{i}\delta_{l_j})$, and $G^{ji}_{L_jL_i}$ represents the matrix element of the propagator (usually the free electron propagator) between the i-th and j-th atoms. Eq. (1) is very important in distinguishing the chemical information from the structural information, the former is held in the T-matrix while the latter is exclusively contained in G. In other words, if one changes the chemical species in the system, only the diagonal matrix T will be affected while the purely off-diagonal matrix G is left unchanged. On the contrary, with atom moving, G will change, but not T. There are two ways to compute the scattering path operator

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1) E-mail: zhaohf@ihep.ac.cn, haifeng.zhao@univ-rennes1.fr
2) Communicator,E-mail: wuzy@ihep.ac.cn
3) E-mail: didier.sebilleau@univ-rennes1.fr

$\tau^{ji}_{L_jL_i}$. The first method is to build the MS matrix $[T^{-1}+G]$ and then to take its inverse numerically. This method is called full MS method. In the second method, the inverse $(I+TG)^{-1}$ in Eq. (1) is expanded as $(I+TG)^{-1}=I+(-1)TG+(-1)^2TGTG+\cdots$ and then is truncated at a desired scattering order. This method is usually referred as MS series expansion method, and its accuracy depends on the truncated scattering order. The advantages and drawbacks of these two methods are clear. In the full MS method, the whole scattering matrix has to be built before taking the inverse, then the size of the matrix (limited by the computer memory available) is the ultimate limit of the method. In the series expansion method, on the contrary, there is no memory limit, but all the photoelectron paths should explicitly be included. Thus the number of the paths and the number of angular momentum values grow fast and the CPU time needed becomes the computing time limit of the approach. We give an example to show the difference of the two methods. In the case of using standard spherical wave basis, the wave functions of the atoms can be expanded with respect to the angular momentum. The expansion can be truncated to a value $l_{\max}$, which can be approximately determined by $\sqrt{l_{\max}(l_{\max}+1)}\sim kr_{\mathrm{m}}$, where k is the wave number of the electron propagating in the system and r_{m} is the radius of the potential sphere of the corresponding atom. As a consequence, the number of possible angular momenta for the expansion around each atom is $(l_{\max}+1)^2$ so that the size of the MS matrix in Eq. (1) is $N_{\mathrm{at}}\times(l_{\max}+1)^2$, where N_{at} is the number of atoms in the system. Because $l_{\max}$ is proportional to k roughly, the dimension of the matrix exquisitely increases with energy. For instance in the case of kinetic energy $\hbar^2k^2/2m\sim 35\mathrm{eV}$, $l_{\max}$ is about 4(actually it also depends on the size of the atoms through r_{m}) and the number of basis functions needed for each atom is about 25. In this case, the full MS calculation is feasible. On the contrary, for a kinetic energy about 1keV, the number of basis functions required to achieve convergence around each atomic site is about 400. The full MS computation in this case is impossible and one has to use the series expansion method. In general, the limit of the first method is at the kinetic energy around 100eV and the number of atoms around 100. Based on this limitation and the fast computer available, one can use the full MS method, otherwise, one has to employ the series expansion approach.

By analyzing these two methods, we find another more efficient MS formulation. In this new method, we expect that a better convergent property for various expansions, which are used to increase the feasibility domain of the full MS method and to reduce the computational time in the MS series expansion method, can be reached. Now, we introduce a general framework in which one can exam whether such a goal can be achieved by using other basis functions instead of standard basis function, such as the spherical wave function or plane wave function.

Although we are presently concentrated on the medium/high energy region where the problem is very serious (as dressed above), searching for better basis is also beneficial to the low energy study. Indeed, in the low energy region, spherical wave function provides a reasonable description of the scattering process because $l_{\max}$ is quite small, however the number of the matrix elements of the propagator, which is important in the MS calculation, is quite large. Therefore, any treatment for reducing this number is welcome.

Finally, to improve the method we can either improve the scattering description so that the number of the elements in the T-matrix can be reduced or reduce the number of terms in the propagator matrix. In this manuscript, we will focus on the first method and will discuss the second method in the forthcoming article. It should be mentioned that for a $N\times N$ block MS matrix, the number of diagonal blocks of the T-matrix is N, while the number of off-diagonal blocks of the G-matrix is $N(N-1)$. Therefore, with the screened KKR method[4] the second method can tremendously be improved by reducing the size of the G-matrix so that the number of atoms used in the full MS method can be increased from 100 to more than 1000[5].

In section 2, in contrary to the normal MS for-

mulism, which is based on the spherical wave basis only, we derive a more generalized formula of the MS theory with an arbitrary basis. In section 3, we present a method for computing matrix elements in the MS theory with a selected basis and discuss how to improve the computation of the scattering process. Finally, summary and conclusion are provided in section 4.

2 MS theory with an arbitrary basis

In the textbook, the hamiltonian of the system can formally be written as

$$H = H_0 + V \ , \tag{2}$$

where H_0 is the hamiltonian of the free electron and V is the potential. The solution of H_0 is generally written as $|\phi_0\rangle$. In the angular momentum representation, $|\phi_0\rangle$ is well-known spherical wave function. Using propagator G

$$G(z) = (z - H)^{-1}, \tag{3}$$

the so-called Dyson equation can be expressed as

$$G = G_0 + G_0 V G = G_0 + G V G_0, \tag{4}$$

or

$$G = G_0 + G_0 T G_0 \tag{5}$$

with transition operator T. Apparently, the Eq. (3) for propagator G is not valid if the interested values of z are those in the continuous spectrum of H. We then have to extend Eq. (3) by approaching to the positive real value of z from either its positive side or its negative side in the complex energy plane. This leads to two G's. One of them is G^+, describing the normal propagation of the particle and the other is G^-, representing the time reversal propagation of the particle.

The second fundamental equation of scattering theory is the Lippmann-Schwinger equation

$$|\psi\rangle = |\phi_0\rangle + G_0 T |\phi_0\rangle. \tag{6}$$

It should be mentioned that the scattering theory found in textbooks is based on the assumption that the potential V in Eq. (2) is relatively short-ranged. For a more generalized framework, we will also include a relatively long-ranged potential. Therefore, expression (2) should be replaced by[6]

$$H = H_{V\infty} + V, \tag{7}$$

where $H_{V\infty}$ is the asymptotical hamiltonian, i.e. the hamiltonian of H at infinity. The eigenstates of the asymptotic hamiltonian were given by Taylor in Ref. [7]. Now, both the Dyson and Lippmann-Schwinger equations should be valid in the more generalized case.

In the case of spherically symmetric potential V, we decompose the Schrödinger equation into a radial part and an angular part. The solution of the latter one is given by spherical harmonics. So the general solution of H can always be written as

$$\psi(\boldsymbol{r}) = \sum\nolimits_L a_L R_l(r) Y_L(\hat{r}), \tag{8}$$

where the subscript $L \equiv (l, m)$ stands for the angular momentum. Therefore, an appropriate basis to be chosen is in the form of

$$\phi_L(\boldsymbol{r}) = \phi_l(r) Y_L(\hat{r}), \tag{9}$$

with a normalization constant being included in the radial part.

Let us start from a new expression

$$H = \bar{H} + \Delta V, \tag{10}$$

where $\bar{H}$ is defined as $H_0 + \bar{V}$ with $\bar{V}$ being a model potential, H_0 stands for the asymptotic hamiltonian, and the remaining potential is $\Delta V = V - \bar{V}$. Apparently, Eq. (2) corresponds to the case of $\bar{V} = 0$. Another useful step is taking a solvable potential $\bar{V}$, in other word, $\bar{H}$ can analytically be solved, so that we can take the eigenstates of $\bar{H}$ as the basis to expand the solution of H. In addition to the solvable Coulomb and harmonic oscillator potentials, the recently developed super-symmetric quantum mechanics (SUSY-QM)[8] provides a variety of solvable potentials. If $|\bar{\phi}\rangle$ is the solution of $\bar{H}$, the Lippmann-Schwinger equation associated to Eq. (10) can be written as

$$|\psi\rangle = |\bar{\phi}\rangle + \bar{G} T_{\Delta V} |\bar{\phi}\rangle, \tag{11}$$

where the $T_{\Delta V}$ operator is related to the potential ΔV by

$$T_{\Delta V} = \Delta V + \Delta V G \Delta V, \tag{12}$$

with G being the full propagator correlated to H and $\bar{G}$ being the propagator associated with $\bar{H}$.

Let us take an arbitrary basis in the partial wave form (because we are considering a spherically symmetric potential)

$$f_L(\boldsymbol{r}) = C_L f_l(r) Y_L(\widehat{r}). \tag{13}$$

We can use such a basis to expand the general solution of $\bar{H}$ (in fact, if $\bar{V}$ is a solvable potential, then the basis $\{|f_L\rangle\}$ can be chosen as the eigenstates of $\bar{H}$) as

$$|\bar{\phi}\rangle = \sum\nolimits_L \bar{A}_L |f_L\rangle. \tag{14}$$

According to the generalized Lippmann-Schwinger equation, the solution of H can be written as

$$|\psi\rangle = \sum\nolimits_L \bar{A}_L [|f_L\rangle + \bar{G} T_{\Delta V} |f_L\rangle], \tag{15}$$

and the matrix of the transition operator $T_{\Delta V}$ on $\{|f_L\rangle\}$ is a diagonal matrix (If $\{|f_L\rangle\}$ are the eigensolutions of $\bar{H}$, the matrix is definitely diagonal, it can be proved from the definition of transition operator (12) as we consider only the case of spherical symmetric potential, for the other basis, the orthogonality of spherical harmonics will also give the diagonal T-matrix)

$$\langle f_{L'} | T_{\Delta V} | f_L \rangle = T_{\Delta V f_L} \delta_{LL'}. \tag{16}$$

Then the solution can be expressed as

$$|\psi\rangle = \sum\nolimits_L \bar{A}_L [|f_L\rangle + \bar{G}|f_L\rangle T_{\Delta V f_L}]. \tag{17}$$

This means that each partial wave in the total wave function is composed by an incoming wave, i.e. the basis function $|f_L\rangle$, and an outgoing scattered wave $\bar{G}|f_L\rangle T_{\Delta V f_L}$. The Eq. (17) also tells us the relative weights between the incoming and outgoing waves. In fact, if $(V - \bar{V})$ goes to zero, $|\psi\rangle$ approaches to $|\bar{\phi}\rangle$ and the second term of the Lippmann-Schwinger Eq. (17) vanishes. This is just what we expected because in this case all the scattering effects have already been included in the basis function. Now, we can directly improve the convergency of the calculation by approaching $\bar{V}$ (when is possible) to V as close as possible.

3 Matrix elements of operators

The MS theory outlined in the introduction shows that the T operator and two propagators G^+ and G^- are sufficient to describe all the MS characteristics and to compute required quantities. In terms of Eq. (1), we can construct the matrix of the scattering path operator. With this matrix, we can calculate the cross-sections of various processes, the electronic and the magnetic properties of the investigated system and, in particular, derive the matrix elements of these operators in an arbitrary basis.

To simplify the notation of Eq. (17), we introduce a quantity $|u_L\rangle = \bar{G}|f_L\rangle$. $|u_L\rangle$ plays the same role of the Hankel function in the spherical-wave-based MS theory. With this notation, we can rewrite Eq. (17) as

$$|\psi\rangle = \sum\nolimits_L \bar{A}_L [|f_L\rangle + |u_L\rangle T_{\Delta V f_L}]. \tag{18}$$

The second term in $\psi(\boldsymbol{r})$ describes the wave function beyond the effective range of the potential $V(r)$ which is short-ranged in comparison with the long-ranged potential $\bar{V}(r)$ in the MS theory. Inside the potential sphere of $V(r)$, we can numerically solve the Schrödinger equation as usual. Assuming that the solution can also be written as

$$\psi(\boldsymbol{r}) = \sum\nolimits_{\bar{L}} \bar{K}_{\bar{L}} R_{\bar{l}}(r) Y_{\bar{L}}(\widehat{r}), \tag{19}$$

$\bar{K}_{\bar{L}}$ is the coefficient of partial wave of order $\bar{L}$. We can match the Eqs. (18) and (19) and their first derivatives, respectively, at the surface of the potential sphere $r = r_{\mathrm{a}}$ to ensure the continuity of both $\psi(\boldsymbol{r})$ and $\psi'(\boldsymbol{r})$ across the potential sphere. Multiplying $Y^*_{L'}(\widehat{r}\,)$ to two conditions and integrating over $\widehat{r}$, we obtain continuity equations for each partial wave

$$\begin{aligned} K_L R_l(r)_{r=r_{\mathrm{a}}} &= \bar{A}_l [f_l(r)_{r=r_{\mathrm{a}}} + u_l(r)_{r=r_{\mathrm{a}}} T_{\Delta V f_L}], \\ K_L R'_l(r)_{r=r_{\mathrm{a}}} &= \bar{A}_l [f'_l(r)_{r=r_{\mathrm{a}}} + u'_l(r)_{r=r_{\mathrm{a}}} T_{\Delta V f_L}]. \end{aligned} \tag{20}$$

Apparently, this equation can easily be solved. In terms of the definition of Wronskian

$$W[a,b] = a(r)\frac{\mathrm{d}b(r)}{\mathrm{d}r} - b(r)\frac{\mathrm{d}a(r)}{\mathrm{d}r}, \tag{21}$$

we finally obtain

$$T_{\Delta V f_L} = -\frac{W[f_l, R_l]_{r=r_{\mathrm{a}}}}{W[u_l, R_l]_{r=r_{\mathrm{a}}}}\,. \tag{22}$$

It is easy to show that if we take the spherical wave basis and $\bar{V}=0$, the Eq. (22) can be reduced to the well-known expression

$$T_{\Delta V f_L}=\mathrm{i}\frac{W[j_l,R_l]_{r=r_\mathrm{a}}}{W[h_l^{(1)},R_l]_{r=r_\mathrm{a}}}. \tag{23}$$

Generally, computing the matrix elements of $\bar{G}^{ji}_{L_jL_i}$ is rather complicated, because $\bar{G}^{ji}_{L_jL_i}$ contains not only the propagator $\bar{G}$ but also the translation operator T, both of which are the functions of the coordinate vector between the atom i and the atom j and the corresponding quantum numbers of angular momenta. However, from the structure of $\bar{G}^{ji}_{L_jL_i}=\langle f_{L_j},j|\bar{G}|f_{L_i},i\rangle$, it is clear that $u_L(\boldsymbol{r})=\langle\boldsymbol{r}|\bar{G}|f_L\rangle$ is the key for the computation of the matrix element. With the obtained T-matrix elements in Eq. (22), the matrix element $\bar{G}^{ji}_{L_jL_i}$ can be calculated. Now, we restrict ourselves to a set of basis, with which $u_L(r)$ can easily be computed. Up to now, we have not selected any basis $\{|f_L\rangle\}$ that will be used to expand the eigenfunction $|\bar{\phi}\rangle$ of $\bar{H}$. Assume that $|f_L\rangle$ is an eigenfunction of $\bar{H}$. In this case, because $\bar{G}$ and $\bar{H}$ commute to each other, it is easy to check that $|u_L\rangle=\bar{G}|f_L\rangle$ is another eigenfunction of $\bar{H}$ with the same eigenvalue. Although we will not prove it here, we claim that $|f_L\rangle$ and $|u_L\rangle$ are linearly independent. This argument can be found in many textbooks for the case of $\bar{G}=G_0$ and can easily be proved if $\bar{V}$ is a Coulomb potential. Moreover, $|f_L\rangle$ and $|u_L\rangle$ should have different asymptotic behaviors at infinity because of the operation of $\bar{G}$ (a detailed proof will be shown in our forthcoming publication).

Using $|u_L\rangle$, we can easily obtain a separable expression of $\bar{G}$ in the following

$$\bar{G}=\sum\nolimits_L|u_L\rangle\langle f_L|\ , \tag{24}$$

and the corresponding Green function $\bar{G}(\boldsymbol{r}',\boldsymbol{r})=\langle\boldsymbol{r}'|\bar{G}|\boldsymbol{r}\rangle$ in the form of

$$\bar{G}(\boldsymbol{r}',\boldsymbol{r})=\sum\nolimits_L u_L(r_M)f_L^{\mathrm{CC}}(r_\mathrm{m}), \tag{25}$$

where "CC" stands for complex conjugate and $\boldsymbol{r}_\mathrm{m}(\boldsymbol{r}_M)$ is the smaller coordinate (larger coordinate) between $\boldsymbol{r}$ and $\boldsymbol{r}'$. Similar to the free electron case, where we choose $f_L(\boldsymbol{r})$ to be the regular function at the origin while $u_L(\boldsymbol{r})$ to be the irregular one, this distinction is made just for the convergent purpose. In the case of $\bar{V}=0$, with spherical wave basis, $u_L(\boldsymbol{r})$ can be written as $-\mathrm{i}\sqrt{\frac{\pi}{2}}i^l h_l^{(1)}(kr)Y_L(\hat{r}\,)$ if the normalized basis function is defined as $k\sqrt{\frac{2}{\pi}}i^l j_l(kr)Y_L(\hat{r}\,)$[9]. Using the same contour integration method described in Ref. [9], we can derive the expression of $u_L(\boldsymbol{r})$. Usually, if we know the regular solution $f_L(\boldsymbol{r})$ of the Schrödinger equation with potential $\bar{V}$, it is easy to derive corresponding irregular solution $g_L(\boldsymbol{r})$. In the Coulomb potential case, the irregular solution has already been given in many textbooks, for instance. Ref. [10]. Assuming that $g_L(\boldsymbol{r})$, as the irregular solution, approaches to $i^l n_l(r)Y_L(\hat{r}\,)$ when $\bar{V}$ goes to zero, we can construct two linearly independent solutions

$$\begin{aligned}u_L^{(1)}(\boldsymbol{r})&=\ f_L(\boldsymbol{r})+\mathrm{i}g_L(\boldsymbol{r}),\\ u_L^{(2)}(\boldsymbol{r})&=\ f_L(\boldsymbol{r})-\mathrm{i}g_L(\boldsymbol{r}).\end{aligned} \tag{26}$$

By performing contour integration and expanding $\langle\boldsymbol{r}|\bar{G}|f_L\rangle$ in terms of the basis function adopted from the eigenfunction of $\bar{H}$, the propagator matrix element $\bar{G}^{ji}_{L_jL_i}$can be calculated by the auxiliary basis function $u_L^{(1)}(\boldsymbol{r})$

$$\langle\boldsymbol{r}|\bar{G}|f_L\rangle=-\mathrm{i}\sqrt{\frac{\pi}{2}}i^l u_l^{(1)}(kr)Y_L(\hat{r}). \tag{27}$$

Up to now, all the multiple scattering matrices can be calculated by using the $\{|f_L\rangle\}$ basis.

4 Discussion and conclusion

We presented here a more generalized framework for the MS calculation. This framework is based on the scattering theory valid for an arbitrary basis, which can be reduced to the spherical wave based standard MS theory. The proposed treatment improves the scattering description by transferring short-ranged scattering effects into the basis functions.

The basis function constructed by using the introduced method may make the convergence of the expansion of the scattered wave function faster. The MS matrix defined in Eq. (1) allows us to use a smaller set of T-matrix blocks than that in the case of using spherical wave basis in the computation. It should

be mentioned that the T-matrix in this framework is slightly different with that in the spherical wave basis case, because the former one is related to the potential $\bar{V}$, while the latter one is associated with the true potential V. In this paper, we have not considered the behavior of the basis functions with respect to the propagator matrix. A more accurate description of the basis function that would substantially decrease the size of the propagator matrix exceeds the scope of the present contribution and will be discussed in the forthcoming publication.

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广义基的多重散射理论*

赵海峰[1;1)] 吴自玉[1;2)] Sebilleau Didier[2;3)]

1 (中国科学院高能物理研究所北京同步辐射装置 北京 100049)

2 (Equipe de Physique des Surfaces et des Interfaces, Laboratoire de Physique des Atomes, Lasers, Molécules et Surfaces, UMR CNRS-Université 6627, Université de Rennes 1, 35042 Rennes Cédex, France)

摘要 提出了任意函数基表象中的多重散射理论. 基于这个框架, 一组新基的多重散射计算表明其收敛性比传统的球谐函数基的要好, 从而可以实现更快和更节省物理内存的计算. 另外, 将多重散射矩阵分为传播矩阵和散射矩阵, 很好地描述了散射性质和减小了多重散射计算中块矩阵的尺寸.

关键词 多重散射理论 基函数 算子 计算

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1) E-mail: zhaohf@ihep.ac.cn, haifeng.zhao@univ-rennes1.fr

2) 通讯作者,E-mail: wuzy@ihep.ac.cn

3) E-mail: didier.sebilleau@univ-rennes1.fr