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Correlation expansion: a powerful alternative multiple scattering calculation method

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Abstract

We introduce a powerful alternative expansion method to perform multiple scattering calculations. In contrast to standard MS series expansion, where the scattering contributions are grouped in terms of scattering order and may diverge in the low energy region, this expansion, called correlation expansion, partitions the scattering process into contributions from different small atom groups and converges at all energies. It converges faster than MS series expansion when the latter is convergent. Furthermore, it takes less memory than the full MS method so it can be used in the near edge region without any divergence problem, even for large clusters. The correlation expansion framework we derive here is very general and can serve to calculate all the elements of the scattering path operator matrix. Photoelectron diffraction calculations in a cluster containing 23 atoms are presented to test the method and compare it to full MS and standard MS series expansion.

1. Introduction

In the last 30 years or so, multiple scattering (MS) theory has achieved great success in the understanding of the physical structure and chemical surroundings in systems belonging to many scientific fields [1, 2]. The basics of the theory relies on the precise description of the different scattering processes undergone by an electron (or any other particle) when moving into a material composed of numerous atoms. Many properties of the system under study, such as the geometric surroundings and the electronic structure, can be modeled with this theory and most of the standard spectroscopies used to extract information from such materials can be shown to be easily described by MS theory [3].

The whole MS theory can be conveniently formulated in terms of the scattering path operator [4] $\tau^{ji}_{L_j L_i}$, which describes all the possibilities for a wavefunction of angular momentum $L_i \equiv (l_i, m_i)$ centered on atom i to reach atom j with angular momentum L_j. The scattering path operator τ^{ji}, connecting the two atoms i and j, can be shown to be the inverse of

$$\tau^{ji} = \left[\left(T^{-1} - G_0\right)^{-1}\right]^{ji} \qquad (1.1)$$

where T is the T-matrix satisfying $[T]^{ji}_{L_j L_i} = -2\frac{k}{\pi} t_{L_j L_i} \delta_{ji}$ for normalized spherical waves. When a spherically symmetric potential is used, $t_{L_j L_i}$ will reduce to $t_{l_j} \delta_{L_j L_i}$. It is related to the phase shifts δ_{l_j} of the potential V_j corresponding to atom j through the relation $t_{l_j} = \sin\delta_{l_j} \exp(\mathrm{i}\delta_{l_j})$; $(G_0)^{ji}_{L_j L_i}$ is the matrix element of the reference propagator (the free electron propagator if V_j is the atomic potential) between the two sites j and i from channel L_i to L_j.

For a given cluster of atoms, there are two basic ways to compute the matrix elements $\tau^{ji}_{L_j L_i}$ needed by MS theory. One is to build the MS matrix $[T^{-1} - G_0]^{ji}_{L_j L_i}$ and to invert it numerically; this is called full MS. It includes all the scattering contributions and is exact from the point of view of scattering theory. This can be done for any energy. The MS matrix, however, has to be built up prior to the inversion and, as no approximation can be used to speed up the computation or to reduce the size of the matrix, the rapidly increasing computation time (which scales as the cube of the dimension of the matrix) and memory (which scales as the square of the dimension of the matrix) will soon limit the use of the method. The second approach consists in expanding the inverse in (1.1) by rewriting it as $\tau^{ji} = [T(I - G_0T)^{-1}]^{ji}$ and truncating the expansion of $(I - G_0T)^{-1}$ to a value called the scattering order,

$$\begin{aligned}\tau^{ji} &= \chi_1^{ji} + \chi_2^{ji} + \cdots + \chi_m^{ji} + \cdots \\ &= T^j\delta_{ji} + T^jG_0^{ji}T^i\left(1-\delta_{ji}\right) \\ &\quad + \sum_{k\neq j,k\neq i} T^jG_0^{jk}T^kG_0^{ki}T^i \\ &\quad + \sum_{m\neq i,k\neq m,\,j\neq k} T^jG_0^{jk}T^kG_0^{km}T^mG_0^{mi}T^i + \cdots \qquad (1.2)\end{aligned}$$

where χ_m^{ji} is called the m-order signal [5] and gives the contribution of the electron after m scattering events. Here, we have omitted the indices of $L \equiv (l, m)$ for simplicity. This method is usually referred to as MS series expansion (SE), or Watson series expansion in the nuclear physics literature [6]. MS series expansion is more flexible than full MS: truncation, filtering or alternative formulations such as the Rehr–Albers (RA) separable representation [7] can be used to speed up while controlling the accuracy of the computation. It has no real memory limitation, but it converges to the matrix inversion (MI) result only when the eigenvalues of the MS matrix are all less than unity, which is not the case in the low energy region. For some clusters, the divergence energy could be as large as 100 eV [8]. Moreover, the series expansion implies the explicit building of all the paths that the particle can follow to go from one atom to another. The number of these paths and the number of angular momentum values can soon become so high that the CPU time needed will seriously limit the usefulness of the method [9].

A few other kinds of methods have been proposed to compute the matrix elements $\tau^{ji}_{L_jL_i}$, such as recursion methods based on a Lanczos/continued fraction (CF) approach [10] or on a Lanczos/LU approach [11], a repartitioning approach [12] and iterative approaches [13], which can provide substantial improvements to the conventional LU (lower–upper) decomposition. However, most of them are still based on the two basic treatments presented above, and as a consequence they share their advantages and disadvantages. Moreover, some of these methods are specifically designed for x-ray absorption spectroscopy calculations, where only the element $\tau^{00}_{L_0L_0}$ is calculated, which usually greatly simplifies the computation. A general efficient method allowing the accurate computation of all the elements of the scattering path operator matrix is therefore required. For instance, core level photoelectron diffraction requires the knowledge of the $\tau^{j0}_{L_jL_0}$ elements, while for low energy electron diffraction (LEED) or valence photoelectron diffraction all the $\tau^{ji}_{L_jL_i}$ values are needed [3].

We introduce here an alternative MS calculation method called the correlation expansion (CE), which was first presented by Ernst *et al* [14] and later described in more details by Siciliano and Thaler [15] in the case of multiple scattering in nuclear physics. An approximate version of it, specifically designed for the case of x-ray absorption, has also been worked out by Filipponi and coworkers [5]. Although an expansion method itself, it is different from the treatment of the MS series expansion where the scattering contributions are grouped by scattering orders. This correlation method partitions the scattering contributions in terms of the contribution from different groups of atoms. Moreover, it is a finite expansion whose full sum is, by construction, always and exactly the matrix inverse $(I - G_0T)^{-1}$. This is demonstrated in the general case in appendix B of [15]. The correlation expansion has the advantages of both full MS and MS series expansion. Like full MS, it can be used in the low energy region without divergence problem, as we demonstrate it numerically in section 3 below. This property comes from the fact that it is based on a combinatorial and finite expansion and not on perturbation theory [15] like MS series expansion. However, like the series expansion method, truncation, filtering or other treatments commonly used in the perturbative expansion can be adapted and applied to optimize the correlation expansion. Furthermore, like the series expansion, the memory requirements should be much less than for full MS, and therefore larger clusters could be computed within the correlation expansion.

We present in section 2 a detailed description of the correlation expansion framework. Within this framework, photoelectron diffraction tests with a 23 atom cluster are presented in section 3. They show the efficiency of the correlation expansion method for MS calculations. Comparisons with the full MS and with the MS series expansion are explicitly shown. A discussion of the advantages and the drawbacks of correlation expansion is given in section 4.

2. Correlation expansion framework

The formal derivation of correlation expansion has been given by Siciliano and Thaler [15] and we recall briefly here the central result of their work. They demonstrate that if A is an operator depending on the N quantities $i, j, k, \ldots$, and if we write as $A^{(ijk)}$ the restriction of A to the subsystem composed of i, j and k, then the following combinatorial expansion holds:

$$\begin{aligned}A &= A^{(i,j,k,\ldots)} \\ &= \sum_i A^{(i)} + \sum_{i\neq j}\left[A^{(i,j)} - A^{(i)} - A^{(j)}\right] \\ &\quad + \sum_{i\neq j,j\neq k}[A^{(i,j,k)} - A^{(i,j)} - A^{(i,k)} - A^{(j,k)} \\ &\quad + A^{(i)} + A^{(j)} + A^{(k)}] + \cdots \\ &= A_1 + A_2 + A_3 + \cdots A_N. \qquad (2.1)\end{aligned}$$

Such an expansion is not unique; there is an infinity of manners to define the subsystem quantities $A^{(ijk)}$, the only constraint being that $A = A^{(i,j,k,\ldots)}$. Equation (2.1) shows that correlation expansion is a finite expansion; the number of terms of this expansion corresponds to the size of the problem. We will now apply this result to the scattering path operator.

We consider a system with N atoms. The scattering path operator τ^{ji} includes all the scatterings from atom i to atom j. Applying equation (2.1) to τ^{ji} for the N atom system leads directly to

$$\tau^{ji} = \gamma_1^{ji} + \gamma_2^{ji} + \cdots + \gamma_m^{ji} + \cdots + \gamma_N^{ji} \tag{2.2}$$

where γ_m^{ji} is the scattering contribution from all possible m atom groups and is called the m body signal. It is the sum of all possible specific m atom group scattering contributions,

$$\gamma_m^{ji} = \sum_{\{k,\ldots,l\}\neq\{i,j\}} \gamma_m^{ji}(k,\ldots,l) \tag{2.3}$$

where $\gamma_m^{ji}(k,\ldots,l)$ is the scattering signal starting from atom i, ending at j and involving the specific $m-2$ atoms $\{k,\ldots,l\}$ when $i \neq j$ or the $m-1$ atoms $\{k,\ldots,l\}$ when i and j coincide.

The treatment of the scattering signal $\gamma_m^{ji}(k,\cdots,l)$ is the key of correlation expansion and differs from the MS series expansion approach. Obviously, the scattering contribution from one atom can only be

$$\gamma_1^{ji} = T^j \delta_{ji}. \tag{2.4}$$

The contribution from the two atom group $\{i, j\}$ is given by

$$\gamma_2^{ji} = \tau_2^{ji} \tag{2.5}$$

where τ_2^{ji} is the scattering path operator matrix element for the two atom cluster $\{i, j\}$. Here, we have set $j \neq i$ and therefore the two extra terms given by equation (2.1) disappear. It is possible to write it as a MS series expansion representation (provided the latter converges) as

$$\begin{aligned}\gamma_2^{ji} &= T^j G_0^{ji} T^i + T^j G_0^{ji} T^i G_0^{ij} T^j G_0^{ji} T^i \\ &\quad + T^j G_0^{ji} T^i G_0^{ij} T^j G_0^{ji} T^i G_0^{ij} T^j G_0^{ji} T^i + \cdots.\end{aligned} \tag{2.6}$$

This MS series expansion contains an infinity of terms. Hence, correlation expansion can be seen as a reordering of the series expansion (reordering of a diverging series is often a standard way to remove the divergence by incorporating into the new series, before it is truncated at the terms that cause the divergence of the original series). For a given cluster of atoms series expansion is an infinite expansion, but at each order the corresponding contribution contains a finite number of terms (the number of paths at this order). By contrast, correlation expansion is a finite expansion but the contribution of each order contains an infinite number of terms such as (2.6). A view such as (2.6) however is only valid when the kernel matrix G_0T has all its eigenvalues within the disc of radius 1, while correlation expansion itself is always valid. So we take here the scattering path operator τ_m^{ji} of small atom groups as the basic calculation unit and choose a suitable way to do the calculation.

The scattering contribution starting from atom i ending at atom j in a given m-atom system is denoted as $\tau_m^{ji}(k,\ldots,l)$. It is the sum of all the contributions involving the atoms $(k,\ldots,l)$,

$$\begin{aligned}\tau_m^{ji}(k,\ldots,l) &= \gamma_m^{ji}(k,\ldots,l) \\ &\quad + \sum_{\{k',\ldots,l'\}\subseteq\{k,\ldots,l\}} \gamma_{m-1}^{ji}\left(k',\ldots,l'\right) \\ &\quad + \sum_{\{k'',\ldots,l''\}\subseteq\{k,\ldots,l\}} \gamma_{m-2}^{ji}\left(k'',\ldots,l''\right) \\ &\quad + \cdots \sum_{\{k'''\}\subseteq\{k,\ldots,l\}} \gamma_3^{ji}\left(k'''\right) + \gamma_2^{ji}\end{aligned} \tag{2.7}$$

where the m-body signal in sub-cluster $\{i, j; k,\ldots,l\}$ is

$$\begin{aligned}\gamma_m^{ji}(k,\ldots,l) &= \tau_m^{ji}(k,\ldots,l) \\ &\quad - \sum_{n=2}^{m-1} \sum_{\{k',\ldots,l'\}\subseteq\{k,\ldots,l\}} \gamma_n^{ji}\left(k',\ldots,l'\right).\end{aligned} \tag{2.8}$$

Equation (2.8) is the equivalent of equation (2.2) when restricting the cluster to the corresponding sub-cluster. Therefore, the total m-body signal is

$$\begin{aligned}\gamma_m^{ji} &= \sum_{\{k,\ldots,l\}\neq\{i,j\}} \tau_m^{ji}(k,\ldots,l) \\ &\quad - \sum_{n=2}^{m-1} \sum_{\{k,\ldots,l\}\neq\{i,j\}} \sum_{\{k',\ldots,l'\}\subseteq\{k,\ldots,l\}} \gamma_n^{ji}\left(k',\ldots,l'\right) \\ &= \sum_{\{k,\ldots,l\}\neq\{i,j\}} \tau_m^{ji}(k,\ldots,l) \\ &\quad - \sum_{n=2}^{m-1} C_{N-n}^{m-n} \sum_{\{k',\ldots,l'\}\neq\{i,j\}} \gamma_n^{ji}\left(k',\ldots,l'\right)\end{aligned} \tag{2.9}$$

where $C_N^M = \frac{N!}{M!(N-M)!}$ is a binomial coefficient [16], with the notation

$$\sum_{\{k',\ldots,l'\}\neq\{i,j\}} \gamma_n^{ji}\left(k',\ldots,l'\right) = \gamma_n^{ji}. \tag{2.10}$$

To further simplify the notation, we can express the m-body signal by recursion,

$$\gamma_m^{ji} = \mathrm{T}_m^{ji} - \sum_{n=2}^{m-1} C_{N-n}^{m-n} \gamma_n^{ji} \tag{2.11}$$

where

$$\mathrm{T}_m^{ji} = \sum_{\{k,\ldots,l\}\neq\{i,j\}} \tau_m^{ji}(k,\ldots,l). \tag{2.12}$$

The same discussion also holds for the case $j = i$. Finally, the m-body signal in the correlation expansion can be expressed as

$$\gamma_m^{ji} = \begin{cases} T^j \delta_{ji} & m = 1 \\ \mathrm{T}_m^{ji} - \displaystyle\sum_{n=1}^{m-1} C_{N-n}^{m-n} \gamma_n^{ji} & m \geqslant 2 \end{cases} \tag{2.13}$$

with T_m^{ji} given by (2.12).

A compact general formula can be obtained by iterating the correlation expansion term γ_m^{ji} in equation (2.11). This gives

$$\gamma_m^{ji} = \sum_{n=1}^{m} P(n,m)\, \mathrm{T}_n^{ji} \tag{2.14}$$

with

$$P(n,m) = \begin{cases} 1 & m = n \\ -\sum_{l=n}^{m-1} C_{N-l}^{m-l} P(n,l) & m > n. \end{cases} \quad (2.15)$$

Introducing the notation

$$Q(n) = \sum_{m=1}^{N} P(n,m) \quad (2.16)$$

to simplify the expression, the scattering path operator is now given by

$$\tau^{ji} = \gamma_1^{ji} + \gamma_2^{ji} + \cdots + \gamma_m^{ji} + \cdots + \gamma_N^{ji} = \sum_{n=1}^{N} Q(n) \mathrm{T}_n^{ji}. \quad (2.17)$$

The correlation expansion framework we have derived here is very general and relatively simple. It allows us to calculate all the elements in the scattering path operator matrix and a convenient algorithm can easily be designed from equations (2.14) or (2.17). Practically speaking, the different terms γ_m^{ji} occurring in these equations are computed by matrix inversion for all the small atom groups appearing in equation (2.12). By using the small atom group scattering path operator matrix instead of the scattering path unit $G_0 T$ as the basic calculation unit, there is no divergence problem in the low energy domain (see the next section for a numerical proof), where, for a given cluster, it always converges to the result obtained by numerically inverting the MS matrix. Therefore, correlation expansion can be viewed as an extreme case of matrix partitioning. Furthermore, as it does not involve the computing of large inverse matrices, it can be applied to large systems where full MS cannot be used. This means that it will have the advantages of both full MS and MS series expansion.

3. Computation tests

In this section, we perform several tests to assess the efficiency and accuracy of correlation expansion within the framework described in section 2. The machine used for these tests was equipped with a four-core Intel Xeon 2.33 GHz processor, but only one core was used in our calculations. We have chosen for these tests to perform photoelectron diffraction spectroscopy (PED) with a cluster of 23 atoms. The choice of PED is dictated by the fact that it involves the contribution of many more matrix elements of the scattering path operator than in the case of x-ray absorption (XAS). Therefore, it leads to much longer calculations, and convergence for the MS series expansion is not as fast as in the case of XAS. From an MS point of view, it can hence be considered as a medium case between the simpler XAS calculations and the more demanding LEED ones. The small size of the cluster is chosen so as to be always able to perform full MS calculations, which will serve as our reference calculations. It has however the disadvantage of reducing the importance of MS. We have also done these test calculations at different energies to be able to encompass both the divergence and convergence domains of the MS series expansion method. We present here a comparison between the three methods, except when series expansion completely diverges, where the results obtained are completely meaningless.

The test cluster chosen is an MgO(001) cluster. It has a hemispherical shape with a magnesium atom located at the origin. Its radius is a, where a is the lattice constant, whose value was taken as 4.210 Å. We selected the magnesium atom located at the bottom as the absorber, so as to maximize MS effects in PED. We chose p core states as the initial states, and a real Hedin–Lundqvist potential was used in the calculation as the optical potential. Furthermore, we have removed all damping (vibrational, mean-free-path-like) from our calculations so that all three methods can be more easily compared. Although damping is the key parameter that controls the convergence of a cross-section in terms of cluster size, our purpose here is not to find a method that would need a smaller cluster to achieve the result, but to propose an alternative approach that will always converge to the MI result for a given cluster (which SE does not always do). Inclusion of damping will certainly improve the rate of convergence of CE in terms of expansion order. For SE, it will both augment the rate of convergence and extend the convergence domain to lower energies. But it will not remove all the divergence problem in SE.

The test energy points are respectively 21, 64, 184 and 289 eV. They correspond to the low energy region (21 eV), where the MS series expansion is expected to diverge (as shown below), the medium energy region (62 eV), where the MS series should converge slowly (at least when damping is included), and a higher energy region (184 and 289 eV), where the full MS method would be time consuming and might be unworkable because of its memory requirements (at least for larger clusters).

3.1. Computation tests: convergence

We present in figures 1–4 the spectra calculated with the correlation expansion for different expansion orders compared to those obtained with the full MS at 21, 62, 184 and 279 eV. The corresponding spectra computed with the MS series expansion for the same orders as for CE are also presented for comparison. We see clearly in these figures that correlation expansion presents good convergence properties at all energy points. In particular, it clearly converges for the low energy point 21 eV, where MS series expansion diverges (we have omitted to plot it at this energy for the higher orders because the calculated signal grows very quickly with the scattering order and is then totally meaningless, as can be seen from the $N = 7$ case). Even very high orders of the SE expansion cannot reproduce the features of the spectrum. We notice as well that, as in the case of the MS series expansion, the lower the energy, the higher the expansion order necessary to achieve a satisfactory convergence for the correlation expansion. Furthermore, CE obviously converges much faster than SE. For instance, in the case of an energy of 184 eV, CE has already converged at order four, while at order seven SE has still not fully converged. This is an important

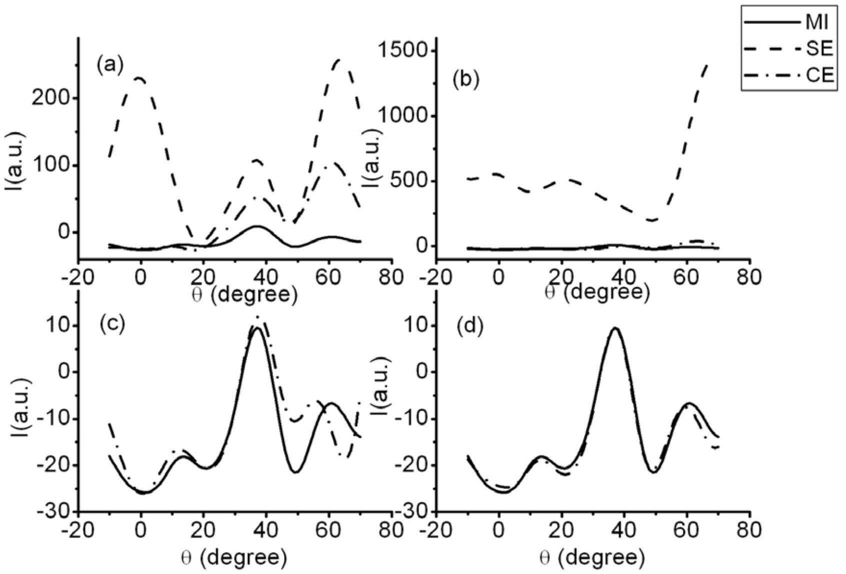

Figure 1. The PED spectra of the MgO cluster (23 atoms) obtained by using the full MS method (MI), MS series expansion (SE) and correlation expansion (CE) at 21 eV. Expansions are truncated at orders 5 (a), 7 (b), 10 (c) and 14 (d). As SE diverges at this energy, SE for truncation orders of 10 and 14 is not plotted in (c) and (d).

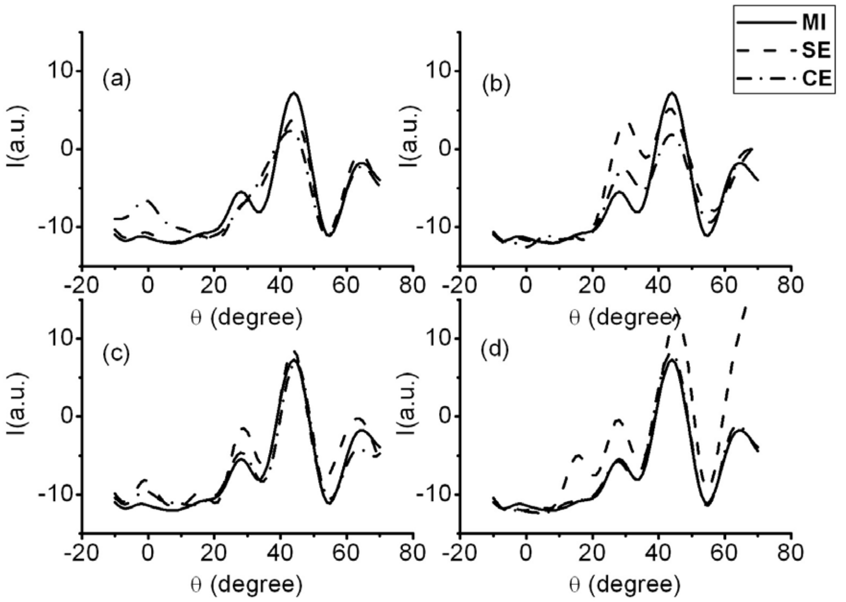

Figure 2. The PED spectra of the MgO cluster (23 atoms) obtained by using the full MS method (MI), MS series expansion (SE) and correlation expansion (CE) at 62 eV. Expansions are truncated at orders 3 (a), 4 (b), 6 (c) and 8 (d).

point because it means, from a practical point of view, that a CE calculation can be truncated much before a SE calculation. This, as we will see, has consequences for the CPU time.

3.2. *Computation tests: accuracy*

By construction, full MS is the most accurate of the three methods as it includes all the scattering contributions, while for the other two, being expansion methods, the accuracy depends on the truncation order. As we saw in section 2, correlation expansion is formally equivalent to full MS when being carried out to the last order of the expansion, because by construction each term at a given order cancels out some terms from the previous order, as can be seen from equation (2.1). As we can see from figures 2–4, the spectra calculated by the correlation expansion method are closer to those obtained by full MS than those resulting from a series expansion calculation at the same truncation order. To compare the calculation accuracy of both the MS series expansion and the correlation expansion methods in a more quantitative way, we consider the spectrum calculated by the full MS method as the reference and define an error function (also known as the R-factor) according to

$$R^{\mathrm{se/ce}} = \frac{\sum_{i=1}^{n} w_i (I_i^{\mathrm{se/ce}} - I_i^{mi})^2}{\sum_{i=1}^{n} w_i (I_i^{mi})^2}$$

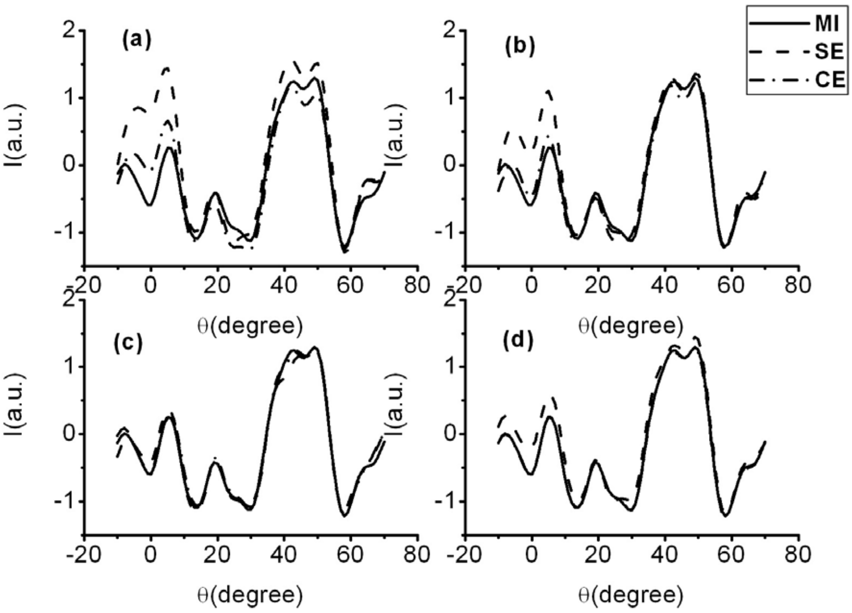

Figure 3. The PED spectra of the MgO cluster (23 atoms) obtained by using the full MS method (MI), MS series expansion (SE) and correlation expansion (CE) at 184 eV. Expansions are truncated at orders 3 (a), 4 (b), 5 (c) and 7 (d).

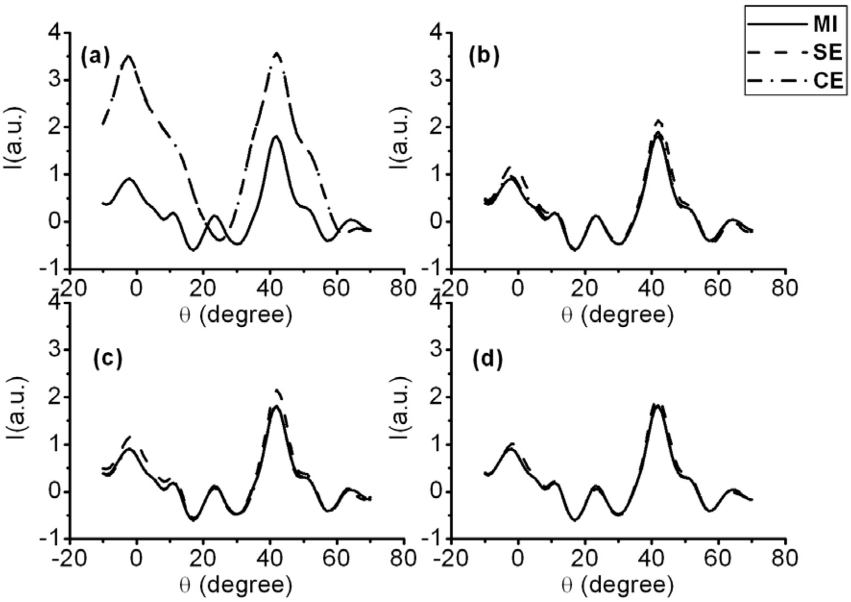

Figure 4. The PED spectra of the MgO cluster (23 atoms) obtained by using the full MS method (MI), MS series expansion (SE) and correlation expansion (CE) at 279 eV. Expansions are truncated at orders 2 (a), 3 (b), 4 (c) and 6 (d).

where $I_i^{mi/\mathrm{se}/\mathrm{ce}}$ is the spectrum calculated with full MS/MS series expansion/correlation expansion at the data point i; w_i is a weight factor which we set here to $w_i = 1$. This definition implies that the smaller the R-factor, the more accurate the calculation based on the corresponding expansion. Figure 5 presents the values of this R-factor for the calculations performed at 184 eV. Here a logarithmic scale is used for the y axis. The important point to note is that the R-factor of correlation expansion is always smaller than that of MS series expansion when the expansions are truncated at the same order. This demonstrates quantitatively that correlation expansion is more accurate than MS series expansion, as we had anticipated qualitatively from a look at the corresponding figure. This result also holds when the calculation is performed at the energies of 62 and 279 eV. MS series expansion strongly diverges at 21 eV and therefore we cannot compare the R-factors. We can also notice in this figure that the R-factor of MS series expansion can sometimes oscillate with the expansion order. This is probably due to the presence of eigenvalues close to unity in the kernel matrix G_0T. This figure shows in particular that, at this energy and for this cluster, CE at order three provides about the same accuracy as SE

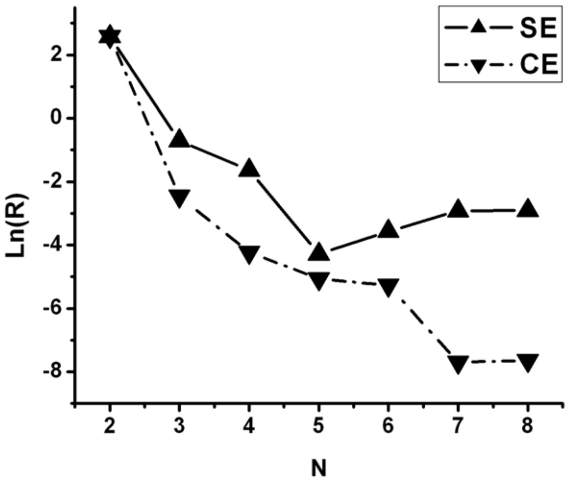

Figure 5. The logarithm of the R-factor of the PED spectrum of the MgO cluster (23 atoms) computed by MS series expansion (SE) and correlation expansion (CE) for different orders at $E = 184$ eV.

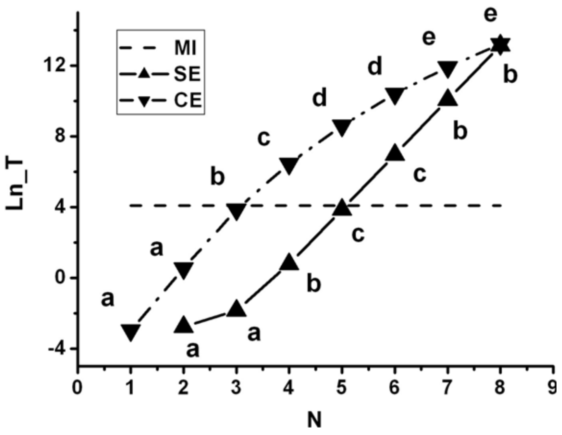

Figure 6. The computation time for the PED calculation of the MgO cluster (23 atoms) computed by the full MS method (MI), MS series expansion (SE) and correlation expansion (CE) for different truncation orders at $E = 184$ eV. The R-factor is also noted to give the accuracies: a, $R > 20\%$; b, $5 < R < 20\%$; c, $1\% < R < 5\%$; d, $0.1\% < R < 1\%$; e, $0.01\% < R < 0.1\%$. A logarithmic scale is used for the y axis.

at order seven or eight. This result can be understood from the respective definition of the expansion terms in MS series expansion and correlation expansion.

Indeed, in the MS series expansion, $\sum_{m=1}^{n} \chi_m^{ji}$ includes all the scattering contributions of order less than or equal to n. These contributions can involve any number of atoms up to n atoms and the number of terms of this truncated expansion is finite. By contrast, in correlation expansion, the m-body signal γ_m^{ji} includes all the scattering events within the sub-clusters built with these m atoms. So, in terms of series expansion, they contain an infinite number of terms. Hence, $\sum_{m=1}^{n} \gamma_m^{ji}$ includes not only the scattering events up to order n, which correspond to $\sum_{m=1}^{n} \chi_m^{ji}$ in MS series expansion, but also all the higher-order terms within the corresponding sub-clusters. This clearly explains why correlation expansion is more accurate than Watson series expansion at the same truncation order. This is exactly what we can see numerically from figures 2–5.

3.3. Computation tests: CPU time and memory

Figure 6 presents the computation time of the PED calculation using MS series expansion and correlation expansion for different truncation orders at 184 eV. The CPU time for full MS is also plotted. As it is the first time that this new correlation expansion framework has been used for a full MS calculation, we have not yet implemented any filtering or other treatments in our computer code to speed up the calculation without losing too much on accuracy. By contrast, for MS series expansion, the RA separable representation, which is widely used in computer codes, already takes into account some approximations (without which MS series expansion would be totally intractable because of the huge number of terms involved in a true SE calculation). We see here that for lower orders correlation expansion takes much more time than MS series expansion for the same truncation order (but the accuracy is different as discussed before). This difference, however, decreases when the expansion order increases: the computation time needed when using MS series expansion increases exponentially with the expansion order (it is roughly proportional to $(N_{\mathrm{at}} - 1)^m$), while that for correlation expansion increases with a slower evolution $(\frac{N_{\mathrm{at}}!}{(N_{\mathrm{at}}-m)!m!})$. Therefore, when the expansion order is larger than a certain order (eight for 184 eV in this cluster), the multiple scattering correlation expansion will take less time than the MS series expansion when truncated at the same order.

Obviously, the computation efficiency depends not only on the computation time but also on the computation accuracy and their interplay. This is why we have added in figure 6 the corresponding R-factor for the different truncation orders. A clearer relation between computation and accuracy is given in figure 7 at the energy of 184 eV. At this energy, the error of a calculation performed by MS series expansion is always larger than 1% ($\ln(1\%) \approx -4.61$). This leads to a visible discrepancy between the spectra obtained by full MS and those by MS series expansion, no matter how high the expansion order is (less than eight in our tests). The accuracy of calculations done by correlation expansion increases with the expansion order (figure 6) and so does the computation time (figure 7). When the CE expansion order is up to five, the R factor is 0.634% and the spectrum is almost indistinguishable from that obtained with full MS method, as shown in figure 3. Unfortunately, the computation time is much more than that required by full MS. So from a computation time point of view, if an error in the calculation of about 5% is acceptable, RA-MS series expansion is faster, although an expansion order of five is needed while it is only four for correlation expansion. If the desired accuracy (here we define it as $1 - R$) has to be larger than 99%, full MS is faster (but we are dealing with a small cluster: for a larger cluster full MS will probably not be possible). This advantage, however, decreases quickly with the increasing energy because of the increasing demand on computer memory for the treatment of the MS matrix and because the expansion order of correlation expansion decreases to obtain the desired accuracy.

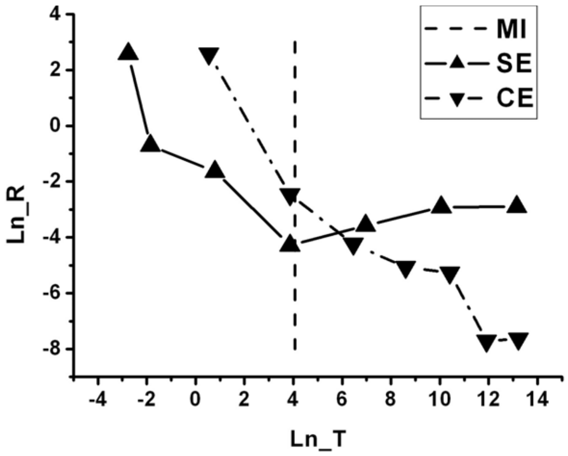

Figure 7. Computation of the error R as a function of the computation time T when the energy is 184 eV. A logarithmic transformation is used for both R and T.

Figures 8–10 show the computation times of our PED calculations at 21, 62 and 279 eV as a function of the expansion order and the accuracy. The trends are similar to those observed at 184 eV: the computation time of MS series expansion increases exponentially with the expansion order (linearly in the figure as a logarithmic scale is used), while that of correlation expansion increases less exponentially; the crossing order is still about eight for these four energy points. In this case, the expansion method that is the fastest will depend essentially on the accuracy needed. The computation time at the crossing point is generally larger than that obtained by full MS, which takes the same time as correlation expansion at order three. Concerning the computation error, it decreases both in MS series and correlation expansion with the energy at the same truncation order, so smaller orders are necessary to achieve the desired accuracy in the high energy calculations, especially for the correlation expansion. An important point to stress here is that, as we can see from the figure 10, correlation expansion already gives a good accuracy when the expansion order is three (less than 1%). There, it takes less time than full MS. At this order, SE has not converged yet and does not give a good agreement with the exact result. To obtain a good agreement with SE, we have to carry it to an order that leads to a CPU time larger than that necessary for CE. Actually, to give an idea of the difference in CPU time, in the case of the 184 eV calculation shown in figure 3, order four CE, which is converged, needs 632 s, while order seven SE, which does not give a fully converged result yet, requires 18 950 s (we recall here that no filtering is used in any of the expansion methods). Order three CE, for which the agreement with the exact result is about the same as that of order seven SE, is obtained after a 47 s calculation. Therefore, when SE does not converge very fast, as is the case in this example, CE has a clear advantage over SE.

Memory usage of the three algorithms we have compared here is quite straightforward and does not require any sophisticated test. Memory is one of the drawbacks of MI and one of the reasons why we propose this correlation expansion approach. By construction, CE relies on the inversion of many small matrices. Therefore, it will evidently cost much less in terms of memory, especially as the same array can be reused for all matrices. SE does not use heavily computer memory, at least when not all the matrix elements of the scattering path operator are needed such as in XAS or PED. We performed some numerical tests that completely confirm this view.

4. Discussion and conclusion

We have introduced and tested a new powerful expansion method to perform MS calculations. In contrast to MS series expansion, where the scattering contributions are grouped in terms of scattering order, correlation expansion partitions the scattering process into contributions from different small atom groups. One of its essential features is that, despite being an expansion, it does converge at all energies, in contrast to series expansion. This results from the fact that it is based on a combinatorial and finite expansion and not on perturbation theory. The general proof for this has been given by Siciliano and Thaler [15]. Therefore, it can be used in the near edge calculation without any divergence problem, where it takes

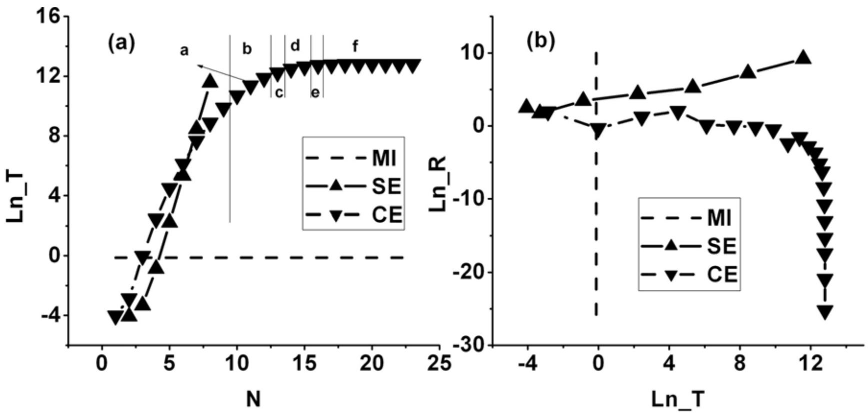

Figure 8. The computation time for the PED calculation of the MgO cluster (23 atoms) computed by the full MS method (MI), MS series expansion (SE) and correlation expansion (CE) for different orders (a) and accuracies (b) at $E = 21$ eV. The logarithm is taken whenever necessary. The R-factor is also noted to give the accuracies in (a): a, $R > 20\%$; b, $5 < R < 20\%$; c, $1\% < R < 5\%$; d, $0.1\% < R < 1\%$; e, $0.01\% < R < 0.1\%$; f, $R < 0.01\%$.

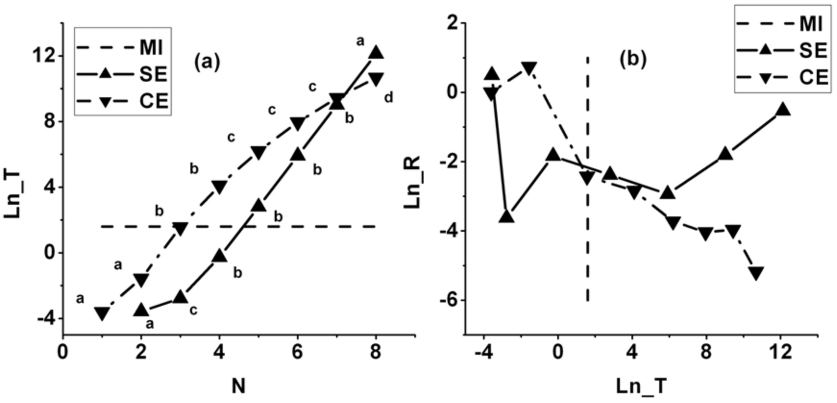

Figure 9. The computation time for the PED calculation of the MgO cluster (23 atoms) computed by the full MS method (MI), MS series expansion (SE) and correlation expansion (CE) for different orders (a) and accuracies (b) at $E = 62$ eV. The logarithm is taken whenever necessary. The R-factor is also noted to give the accuracies in (a): a, $R > 20\%$; b, $5 < R < 20\%$; c, $1\% < R < 5\%$; d, $0.1\% < R < 1\%$.

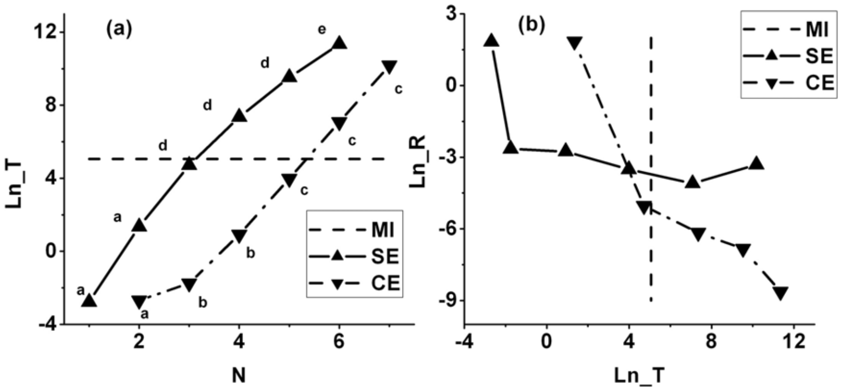

Figure 10. The computation time for the PED calculation of the MgO cluster (23 atoms) computed by the full MS method (MI), MS series expansion (SE) and correlation expansion (CE) for different orders (a) and accuracies (b) at $E = 279$ eV. The logarithm is taken whenever necessary. The R-factor is also noted to give the accuracies in (a): a, $R > 20\%$; b, $5 < R < 20\%$; c, $1\% < R < 5\%$; d, $0.1\% < R < 1\%$; e, $0.01\% < R < 0.1\%$.

much less memory than full MS. A direct consequence is that larger clusters can be considered. It is also the only approach of the three for MS calculations within the energy region where full MS is impossible to use (because of the size of the cluster considered) and where series expansion diverges. In some clusters, this energy can reach the order of 100 eV [8], far away from the divergence limit usually accepted. Furthermore, for series expansion, the larger the cluster, the lower the convergence, as MS becomes more and more important. This can be checked by plotting as a function of energy the spectral radius (i.e. the largest of the eigenvalues) of the kernel matrix. Indeed, preliminary tests show that it does not behave monotonically, but exhibits peaks, which, under certain circumstances (such as the level of damping, the cluster size and the electronic structure), can enter the divergence domain. In particular, the spectral radius seems to increase importantly with the cluster size, which can be understood qualitatively, as the spectral radius is nothing else than a measure of the importance of MS in the system. Moreover, CE is more accurate than MS series expansion when the expansion is taken up to the same order. As we have seen in our 23 atom case, CE in its present version without approximation will be faster than SE each time SE converges slowly, i.e. at medium energies and for large clusters. Furthermore, the CE framework we have outlined here is very general and not limited to certain specific spectroscopies. In particular, it can calculate all the elements in the scattering path operator matrix, and therefore can be used not only for XAS, as in the work by Filipponi *et al* [10], but also for PED where a column block of this matrix is needed, for LEED or valence level PED where all elements are necessary, or all other spectroscopy that can be described within MS theory.

No damping was included in our tests, as vibrational damping is treated in a slightly different way in the RA-SE calculation. Obviously, damping will improve the convergence of the two expansion methods. Therefore, we can expect a decrease of the CPU time in this case as truncation will be possible at a lower order while this will not affect the CPU time of matrix inversion.

In its present form (i.e. inverting exactly all the sub-cluster matrices), correlation expansion is still limited by its computation time although it compares favorably to series expansion. It takes much more time than MS series expansion at the same truncation order, but, as we have demonstrated, the two truncation orders cannot be compared as SE converges much more slowly (and we expect the discrepancy between their respective convergence rates to be much more important for clusters larger than the one we have used for our tests). Some further work is therefore needed to improve its already interesting performances. Such an efficient approximation has been implemented by Filipponi and co-workers in the very particular case of x-ray absorption to speed up correlation expansion where full matrix inversion of the sub-cluster matrices is replaced by a recursive continued fraction approach. There, the approximation after the ith iteration amounts to calculating exactly the cross-section for a finite chain model including $i - 1$ bonds, i.e. the i body signal [10]. This method however is not suitable in the general MS calculation we have developed here, as it works only for the calculation of diagonal elements of an inverse matrix. We are currently working on alternative methods that would allow us to compute all the elements of the inverse matrices without explicitly inverting them. We tested a matrix partition method to perform the calculation of small atom groups, leading to an about 5% time and 10% memory saving. Obviously, our approach at present gives the full contribution at a given order. Possible solutions to speed up the method, especially in view of its high accuracy, which is not always needed, include the introduction of suitable filtering to eliminate sub-cluster matrices whose scattering contribution is negligible, and the replacement of the full inversion of the remaining matrices by an accurate approximation that would be valid in all MS cases. The fact that small cluster MS matrices have a low spectral radius [8] even at very low energies (compared to larger clusters) makes us confident that we will be able to find such a fast alternative to matrix inversion for these small matrices.

Acknowledgments

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References

[1] Rehr J J and Albers R C 2000 *Rev. Mod. Phys.* **72** 621–54
[2] Natoli C R, Benfatto M, Della Longa S and Hatada K 2003 *J. Synchrotron Radiat.* **10** 26–42
[3] Sebilleau D, Gunnella R, Wu Z Y, Di Matteo S and Natoli C R 2006 *J. Phys.: Condens. Matter* **18** R175–230
[4] Gyorffy B L and Stott M J 1973 *Band Structure Spectroscopy of Metals and Alloys* ed D J Fabian and L M Watson (London: Academic) pp 385–403
[5] Filipponi A, Di Cicco A and Natoli C R 1995 *Phys. Rev.* B **52** 15122–34
[6] Watson K M 1953 *Phys. Rev.* **89** 575–87
[7] Rehr J J and Albers R C 1990 *Phys. Rev.* B **41** 8139–49
[8] Sébilleau D and Natoli C R 2008 at press
[9] Zhao H F, Wu Z Y and Sébilleau D 2007 *High Energy Phys. Nuclear Phys.* **31** 452–7
[10] Filipponi A 1991 *J. Phys.: Condens. Matter* **3** 6489–507
[11] Ankudinov A L, Bouldin C E, Rehr J J, Sims J and Hung H 2002 *Phys. Rev.* B **65** 104107
[12] Fujikawa T 1993 *J. Phys. Soc. Japan* **62** 2155–65
[13] Wu H and Tong S Y 1999 *Phys. Rev.* B **59** 1657–60
[14] Ernst D J, Londergan J T, Miller G A and Thaler R M 1977 *Phys. Rev.* C **16** 537–55
[15] Siciliano E R and Thaler R M 1977 *Phys. Rev.* C **16** 1322–32
[16] Abramowitz M and Stegun I A 1972 *Handbook of Mathematical Functions with Formuliasm Graphs, and Mathematical Tables, 10th version* (Washington: US Government Printing Office) chapter 24 (24.1.1) p 822