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New recurrence relations for matrix elements of the propagator

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Abstract. Matrix elements of the propagator in a spherical wave representation are the key quantities in most scattering problems. Here, we review the existing methods to compute them and propose a new one—a set of recurrence relations—which is faster than the currently used ways of calculating them at high energy.

1. Introduction

One of the main problems encountered in the scattering theory in solids is the way to calculate as efficiently as possible the matrix elements of the propagator in a spherical wave representation. These quantities being, together with the t matrices, the essential ingredient of the theory, it is necessary to have a fast and accurate way to compute them. Several approaches have already been proposed to tackle this problem and they can be divided into two categories: direct methods and recursive schemes. We propose here new recurrence relations to calculate these quantities which we believe are faster than those already proposed.

In section 2, we recall the definition of the matrix elements of the propagator and of related quantities. We review in section 3 the various methods (at least those known to us) existing to calculate these matrix elements and discuss them. New recurrence relations are derived in section 4. They are tested both in speed and stability in section 5 and compared to other existing ways of computation.

2. Definitions

Let us consider an outgoing spherical wave of angular momentum $L = (\ell, m)$ centred on an atom i situated at $\boldsymbol{r}_i$ with respect to the origin, and incoming on an atom j located at $\boldsymbol{r}_j$. From partial wave theory [1], we know that such a wave can be represented by the wave function

$$\varphi_L = \mathrm{i}^\ell h_\ell^{(1)}(k|\boldsymbol{r} - \boldsymbol{r}_i|) Y_L(\widehat{\boldsymbol{r} - \boldsymbol{r}_i}) \tag{1}$$

with $h_\ell^{(1)}(kr)$ being a spherical Hankel function of the first kind [2], $Y_L(\hat{\boldsymbol{r}})$ a spherical harmonic and $\hat{\boldsymbol{r}}$ the unit vector in the direction of $\boldsymbol{r}$.

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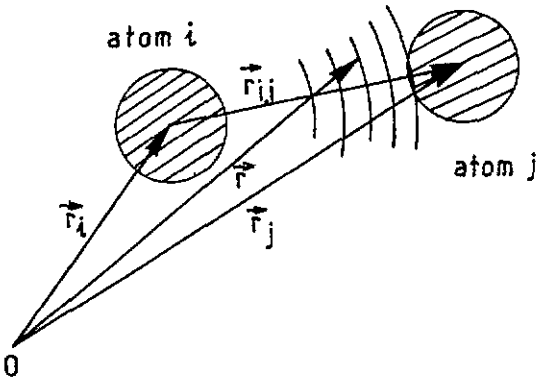

Figure 1. Scattering geometry.

Such a wave cannot be scattered directly by atom i but must be re-expanded first as a linear combination of spherical waves centred on the scatterer:

$$i^{\ell} h_{\ell}^{(1)}(k|r - r_i|) Y_L(\widehat{r - r_i}) = \sum_{L'} G_{L'L}(r_{ij}) i^{\ell'} j_{\ell'}(k|r - r_j|) Y_{L'}(\widehat{r - r_j}) \qquad (2)$$

where $r_{ij} = r_j - r_i$ as defined in figure 1.

The coefficients of the linear combination, which we can write as $G^{ij}_{L'L}$ to simplify the notation, are the matrix elements of the free electron propagator $G_0^+(k)$ taken between state $\langle L', k|$ centred at r_j and state $|k, L\rangle$ centred at r_i.

Relations such as equation (2) are called addition theorems and have been known for some time now [3–5]. Here,

$$G^{ij}_{L'L} = 4\pi \sum_{L''} i^{\ell''} h^{(1)}_{\ell''}(kr_{ij}) Y_{L''}(\hat{r}_{ij}) G(L'L''|L) \qquad (3)$$

with

$$G(L'L''|L) = \int Y_{L'}(\hat{k}) Y_{L''}(\hat{k}) Y^*_L(\hat{k})\, d\Omega_{\hat{k}}. \qquad (4)$$

$G(L'L''|L)$ is a Gaunt coefficient [6] and is usually expressed in terms of Wigner's $3j$ symbols [7] for numerical calculations.

Introducing the Hankel polynomial $c_\ell(kr)$ [2] by

$$i^{\ell} h_{\ell}^{(1)}(kr) = (e^{ikr}/ikr) c_\ell(kr) \qquad (5)$$

i.e. the correction factor to the asymptotic form of the spherical Hankel function, we can write $G^{ij}_{L'L}$ conveniently in terms of its reduced form $\tilde{G}^{ij}_{L'L}$:

$$G^{ij}_{L'L} = 4\pi (e^{ikr_{ij}}/ikr_{ij}) \tilde{G}^{ij}_{L'L}. \qquad (6)$$

We can now rotate the bond direction r_j onto the z axis to take advantage of the fact that z is a quantization axis for the angular momentum. The expression of $\tilde{G}^{ij}_{L'L}$ along the z direction will be therefore much simplified. Introducing the z axis reduced free-electron propagator matrix elements in an angular momentum representation by

$$\tilde{G}_{L'L}(r_{ij}\hat{z}) = \tilde{g}^{ij}_{\ell'\ell}(m)\delta_{mm'} = \sqrt{[(2\ell' + 1)/4\pi][(2\ell + 1)/4\pi]}\, \tilde{h}^{ij}_{\ell'\ell}(m)\delta_{mm'} \qquad (7)$$

and applying rotation matrices [8], we can expand it in magnetic quantum number:

$$\tilde{G}^{ij}_{LL'} = \sum_{\bar{m}} R^{\ell'}_{m'\bar{m}}(\varphi_{ij} - \pi, -\theta_{ij}, 0)\tilde{g}^{ij}_{\ell'\ell}(\bar{m})R^{\ell}_{\bar{m}m}(0, \theta_{ij}, \pi - \varphi_{ij}) \tag{8}$$

where $(\theta_{ij}, \varphi_{ij})$ are the spherical polar coordinates of $\hat{r}_{ij}$.

Writing the Gaunt coefficient in (3) in terms of Wigner's $3j$ symbols [7] leads to

$$\tilde{h}^{ij}_{\ell'\ell}(\bar{m}) = (-1)^{\bar{m}} \sum_{\ell''=|\ell-\ell'|}^{(\ell+\ell')} (2\ell'' + 1)c_{\ell''}(kr_{ij}) \begin{pmatrix} \ell & \ell' & \ell'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & \ell' & \ell'' \\ -\bar{m} & \bar{m} & 0 \end{pmatrix}. \tag{9}$$

It is worth noting that this quantity and the corresponding one for $\tilde{g}^{ij}_{\ell'\ell}(\bar{m})$ do not depend on the sign of $\bar{m}$. From now on we will consequently write them as $\tilde{h}^{ij}_{\ell'\ell}(|\bar{m}|)$ and $\tilde{g}^{ij}_{\ell'\ell}(|\bar{m}|)$. Moreover, $\tilde{h}^{ij}_{\ell'\ell}(|\bar{m}|)$ (and $\tilde{g}^{ij}_{\ell'\ell}(|\bar{m}|)$) is symmetrical with respect to ℓ and ℓ', i.e.

$$\tilde{h}^{ij}_{\ell'\ell}(|\bar{m}|) = \tilde{h}^{ij}_{\ell\ell'}(|\bar{m}|). \tag{10}$$

These two properties are fundamental as they allow us to reduce the number of values to be computed. Furthermore, the set of values of $\bar{m}$ can be most of the time limited to the first few without significant loss of accuracy. The reason for this was argued by Barton and Shirley [5] and more recently by Rehr and Albers [9]. We refer the reader to these references for a comprehensive discussion of the matter.

3. State of the art

The more straightforward way to calculate the matrix elements of the propagator $G^{ij}_{L'L}$ is to make use of their definition (equation (3)). This can be a fast way to do it provided that the Gaunt coefficients have already been tabulated. However, at high energies where many values of the angular momentum indices (ℓ, m) are necessary for the addition theorem (3) to converge, this method can become fastidious as Gaunt coefficients $G(L'L''|L)$ will need a lot of storage place and much time to be computed. One way to circumvent this latter problem is to use a stable recursive scheme such as that proposed by Schulten and Gordon [10] to calculate the $3j$ symbols occurring in the Gaunt coefficient. But this can be still time consuming and will leave unaltered the storage problem.

A better philosophy, at least at high energy, is to find recurrence relations for $G^{ij}_{L'L}$ or to express them in terms of quantities that can be easily calculated by means of a recursion scheme. We review here the various approaches that can be found in the literature.

3.1. Chew's recurrence relations

A general recursion scheme was recently proposed by Chew [11]. Writing

$$\alpha_{L'L} = i^{\ell'-\ell}G^{ij}_{L'L} \tag{11}$$

and introducing

$$\begin{aligned} a^{+}_{L} &= -\sqrt{(\ell + m + 1)(\ell - m + 1)/(2\ell + 1)(2\ell + 3)} \\ a^{-}_{L} &= \sqrt{(\ell + m)(\ell - m)/(2\ell + 1)(2\ell - 1)} \\ b^{-}_{L} &= \sqrt{(\ell - m)(\ell - m - 1)/(2\ell + 1)(2\ell - 1)} \\ b^{+}_{L} &= \sqrt{(\ell + m + 1)(\ell + m + 2)/(2\ell + 1)(2\ell + 3)} \end{aligned} \tag{12}$$

Chew found

$$\begin{aligned} a^{+}_{\ell m}\alpha_{\ell' m',\ell+1 m} &= -a^{-}_{\ell m}\alpha_{\ell' m',\ell-1 m} + a^{+}_{\ell'-1 m'}\alpha_{\ell'-1 m',\ell m} + a^{-}_{\ell'+1 m'}\alpha_{\ell'+1 m',\ell m} \\ b^{+}_{\ell m}\alpha_{\ell' m',\ell+1 m+1} &= -b^{-}_{\ell m}\alpha_{\ell' m',\ell-1 m+1} + b^{+}_{\ell'-1 m'-1}\alpha_{\ell'-1 m'-1,\ell m} + b^{-}_{\ell'+1 m'-1}\alpha_{\ell'+1 m'-1,\ell m} \end{aligned} \tag{13}$$

with the initial value

$$b^{+}_{\ell\ell}\alpha_{\ell' m',\ell+1\ell+1} = b^{+}_{\ell'-1 m'-1}\alpha_{\ell'-1 m'-1,\ell\ell} + b^{-}_{\ell'+1 m'-1}\alpha_{\ell'+1 m'-1,\ell\ell} \tag{14}$$

and the property

$$\alpha_{\ell' m',\ell-m} = (-1)^{m'+m}\alpha^{*}_{\ell'-m',\ell m} \tag{15}$$

which is only valid for real k.

This method to calculate $G^{ij}_{L'L}$ is very appealing and very fast indeed. Unfortunately, the first recurrence relation in (13) becomes unstable at high energy [12]. Moreover, there is no way to truncate the calculation at high energy.

Alternatively, it is possible to focus on $\tilde{h}^{ij}_{\ell'\ell}(|\bar{m}|)$ instead of $G^{ij}_{L'L}$. This is the method favoured by most authors as the development in $\bar{m}$ converges very quickly, especially at high energy.

3.2. The Rehr and Albers approach

One elegant way to find a fast procedure to compute the $\tilde{h}^{ij}_{\ell'\ell}(|\bar{m}|)$ is to use the Rehr and Albers separable representation of the matrix elements of the free-electron propagator [9]. Indeed, if we follow their main result, we can write

$$\tilde{G}^{ij}_{L'L} = \sum_{\bar{m}=-\ell_m}^{+\ell_m}\sum_{n=0}^{n_m}\tilde{A}^{L'}_{\bar{m}n}(z_{ij})A^{L}_{\bar{m}n}(z_{ij}) \tag{16}$$

where the contributions from the L incoming partial waves and from the various L' outgoing partial waves have been separated. Here, $\ell_m = \min(\ell, \ell')$, $n_m = \min(\ell', \ell - |\bar{m}|)$ and $z_{ij} = 1/ikr_{ij}$. The other quantities are given by

$$\begin{aligned} A^{L}_{\bar{m}n}(z_{ij}) &= R^{\ell}_{\bar{m}m}(\hat{r}_{ij} \to \hat{z})(-1)^{|\bar{m}|}\sqrt{[(2\ell+1)/4\pi](\ell-|\bar{m}|)!/(\ell+|\bar{m}|)!}H^{(|\bar{m}|+n)}_{\ell}(z_{ij}) \\ \tilde{A}^{L'}_{\bar{m}n}(z_{ij}) &= R^{\ell'}_{m'\bar{m}}(\hat{z} \to \hat{r}_{ij})\sqrt{[(2\ell'+1)/4\pi](\ell'+|\bar{m}|)!/(\ell'-|\bar{m}|)!}H^{(n)}_{\ell'}(z_{ij}) \end{aligned} \tag{17}$$

where we have defined for convenience

$$H^{(n)}_{\ell}(z) = (z^n/n!)\frac{d^n}{dz^n}(\bar{C}_{\ell}(z)) \tag{18}$$

with $\bar{C}_{\ell}(z) = c_{\ell}(kr)$, the Hankel polynomial of degree ℓ. If we combine (7), (8) and (16), we are led to the important relation

$$\tilde{h}^{ij}_{\ell'\ell}(|\bar{m}|) = (-1)^{|\bar{m}|}\sqrt{\frac{(\ell-|\bar{m}|)!(\ell'+|\bar{m}|)!}{(\ell+|\bar{m}|)!(\ell'-|\bar{m}|)!}}\sum_{n=0}^{\min(\ell',\ell-|\bar{m}|)}H^{(|\bar{m}|+n)}_{\ell}(z_{ij})H^{(n)}_{\ell'}(z_{ij}). \tag{19}$$

$H^{(n)}_{\ell}(z)$ can be computed with the recursion procedure

$$H^{(n)}_{\ell+1}(z) = H^{(n)}_{\ell-1}(z) - (2\ell+1)z[H^{(n)}_{\ell}(z) + H^{(n-1)}_{\ell}(z)] \qquad \text{for } n \in [0, \ell] \tag{20}$$

and the initial values

$$\begin{aligned} H^{(n)}_{n}(z) &= [(2n)!/n!](-z/2)^n \\ H^{(n)}_{n+1}(z) &= H^{(n)}_{n}(z)(2n+1)[1-(n+1)z]. \end{aligned} \tag{21}$$

3.3. Nozawa's recursion scheme

An alternative procedure is to derive directly a recursive scheme to calculate $\tilde{h}^{ij}_{\ell'\ell}(|\bar{m}|)$. This can be donc very simply by using Nozawa's Helmholtz solid harmonics addition theorem coefficient recurrence relations [4]. These solid harmonics are defined by

$$H^{|\bar{m}|}_{\ell'\ell}(kr_{ij}) = \sum_{\ell''=|\ell'-\ell|}^{\ell'+\ell} i^{\ell''}(2\ell''+1)h^{(1)}_{\ell''}(kr_{ij})c^{\bar{m}}_{\ell''\ell'\ell} \tag{22}$$

with

$$c^{m}_{\ell''\ell'\ell} = \frac{1}{2}\int_{-1}^{1} P_{\ell''}(x)P^{m}_{\ell'}(x)P^{m}_{\ell}(x)\,dx. \tag{23}$$

Indeed, with our notations, they can be written as

$$H^{|\bar{m}|}_{\ell'\ell}(kr_{ij}) = (e^{ikr_{ij}}/ikr_{ij})\sqrt{(\ell+|\bar{m}|)!(\ell'+|\bar{m}|)!/(\ell-|\bar{m}|)!(\ell'-|\bar{m}|)!}\,\tilde{h}^{ij}_{\ell'\ell}(|\bar{m}|). \tag{24}$$

His recurrence relations become

$$\begin{aligned}
\tilde{h}^{ij}_{\ell'\ell}(|\bar{m}|+1) &= A\tilde{h}^{ij}_{\ell'\ell}(|\bar{m}|) + ikr_{ij}[B\tilde{h}^{ij}_{\ell'\ell+1}(|\bar{m}|) - C\tilde{h}^{ij}_{\ell'\ell-1}(|\bar{m}|)] \\
\tilde{h}^{ij}_{\ell'+1\ell}(|\bar{m}|) &= -\alpha\tilde{h}^{ij}_{\ell'-1\ell}(|\bar{m}|) + \beta\tilde{h}^{ij}_{\ell'\ell+1}(|\bar{m}|) + \gamma\tilde{h}^{ij}_{\ell'\ell-1}(|\bar{m}|)
\end{aligned} \tag{25}$$

with

$$\begin{aligned}
A &= \sqrt{(\ell-|\bar{m}|)(\ell+|\bar{m}|+1)/(\ell'-|\bar{m}|)(\ell'+|\bar{m}|+1)} \\
B &= [1/(2\ell+1)]\sqrt{(\ell-|\bar{m}|)(\ell-|\bar{m}|+1)/(\ell'-|\bar{m}|)(\ell'+|\bar{m}|+1)} \\
C &= [1/(2\ell+1)]\sqrt{(\ell+|\bar{m}|)(\ell+|\bar{m}|+1)/(\ell'-|\bar{m}|)(\ell'+|\bar{m}|+1)} \\
\alpha &= \sqrt{(\ell'-|\bar{m}|)(\ell'+|\bar{m}|)/(\ell'+|\bar{m}|+1)(\ell'-|\bar{m}|+1)} \\
\beta &= [(2\ell'+1)/(2\ell+1)]\sqrt{(\ell+|\bar{m}|+1)(\ell-|\bar{m}|+1)/(\ell'+|\bar{m}|+1)(\ell'-|\bar{m}|+1)} \\
\gamma &= [(2\ell'+1)/(2\ell+1)]\sqrt{(\ell+|\bar{m}|)(\ell-|\bar{m}|)/(\ell'+|\bar{m}|+1)(\ell'-|\bar{m}|+1)}
\end{aligned} \tag{26}$$

and the initial values $\tilde{h}^{ij}_{0\ell}(0)$ and $\tilde{h}^{ij}_{1\ell}(0)$ given by

$$\begin{aligned}
\tilde{h}^{ij}_{0\ell}(0) &= c_{\ell}(kr_{ij}) \\
\tilde{h}^{ij}_{1\ell}(0) &= \frac{(\ell+1)c_{\ell+1}(kr_{ij}) + \ell c_{\ell-1}(kr_{ij})}{(2\ell+1)}.
\end{aligned} \tag{27}$$

The Hankel polynomials $c_{\ell}(kr)$ may be calculated by means of the recursion relation

$$c_{\ell-1}(kr) - c_{\ell+1}(kr) = [(2\ell+1)/ikr]c_{\ell}(kr) \tag{28}$$

and the initial values

$$\begin{aligned}
c_0(kr) &= 1 \\
c_1(kr) &= 1 + i/kr.
\end{aligned} \tag{29}$$

3.4. Fritzsche's recurrence relations

Recurrence relations for related quantities have also been derived by Fritzsche [13]. In order to compare the two sets of relations, we have to relate his matrix elements of the z axis propagator to ours. The link between the two notations is

$$g^{|\bar{m}|}_{\ell'\ell}(r_{ij}) = i^{\ell'-\ell}(e^{ikr_{ij}}/ikr_{ij})\sqrt{(2\ell+1)(2\ell'+1)}\,\tilde{h}^{ij}_{\ell'\ell}(|\bar{m}|). \tag{30}$$

It can be checked easily that inserting (30) in his equaiton (13) leads exactly to (25*b*). His second relation however is different. It transforms under (30) as

$$\tilde{h}^{ij}_{|\bar{m}|+1\ell}(|\bar{m}|) = \left[\sqrt{2|\bar{m}|+1}/(2\ell+1)\right]\left[\sqrt{(\ell-|\bar{m}|)(\ell+|\bar{m}|)}\,\tilde{h}^{ij}_{|\bar{m}|\ell-1}(|\bar{m}|) + \sqrt{(\ell-|\bar{m}|+1)(\ell+|\bar{m}|+1)}\,\tilde{h}^{ij}_{|\bar{m}|\ell+1}(|\bar{m}|)\right] \tag{31}$$

with the initial value

$$\tilde{h}^{ij}_{|\bar{m}|+1\ell}(|\bar{m}|+1) = \left\{\sqrt{[(2|\bar{m}|+1)/(2|\bar{m}|+2)](\ell-|\bar{m}|)(\ell+|\bar{m}|+1)}\,\frac{1}{ikr_{ij}}\right\}\tilde{h}^{ij}_{|\bar{m}|\ell}(|\bar{m}|). \tag{32}$$

Note that this initial value can be greatly simplified by making use of equation (B8) of [9]. Indeed, we can replace it by

$$\tilde{h}^{ij}_{|\bar{m}|\ell}(|\bar{m}|) = \sqrt{[(\ell+|\bar{m}|)!/(\ell-|\bar{m}|)!](2|\bar{m}|-1)!!/2^{|\bar{m}|}|\bar{m}|!}\,c_\ell(kr_{ij})/(ikr_{ij})^{|\bar{m}|}. \tag{33}$$

Both sets (Nozawa's and Fritzsche's) are complete and therefore any of them may be used to generate the $\tilde{h}^{ij}_{\ell'\ell}(|\bar{m}|)$ necessary for the calculation of the propagator. However, both sets of equations raise the same problem: due to the $\tilde{h}^{ij}_{\ell'\ell+1}(|\bar{m}|)$ term on the right-hand side of equations (25) and (31), the total number of values that have to be calculated is far greater than the number of values explicitly needed. For example, if we want to calculate $\tilde{h}^{ij}_{25\,25}(0)$ by means of equation (B7), we have to carry on the recursion scheme up to $\tilde{h}^{ij}_{0\,50}(0)$! This process will slow down the recursion and it is therefore interesting to seek for new recurrence relations that do not exhibit any incrementation in ℓ or ℓ' on the right-hand side.

Note finally that separable representations of the matrix elements of the Green operator might lead in certain cases (especially for small values of r_{ij} at high energy and when truncating the angular momentum expansion) to inaccuracies. This problem was pointed out very recently by Fritzsche [14] and could be due to the oscillatory nature of the coupling between the two angular momenta L and L'.

4. New recurrence relations

An efficient way to obtain such new relations is to use equation (19) which is the expression of $\tilde{h}^{ij}_{\ell'\ell}(|\bar{m}|)$ in the Rehr–Albers scheme, as a starting point:

$$\tilde{h}^{ij}_{\ell'\ell}(|\bar{m}|) = (-1)^{|\bar{m}|}\sqrt{\frac{(\ell-|\bar{m}|)!(\ell'+|\bar{m}|)!}{(\ell+|\bar{m}|)!(\ell'-|\bar{m}|)!}}\sum_{n=0}^{\min(\ell',\ell-|\bar{m}|)} H_\ell^{(|\bar{m}|+n)}(z_{ij})H_{\ell'}^{(n)}(z_{ij}). \tag{19}$$

As shown in the previous section, the Rehr–Albers functions $H_\ell^{(n)}(z)$ satisfy the recurrence relation

$$H_{\ell+1}^{(n)}(z) = H_{\ell-1}^{(n)}(z) - (2\ell+1)z[H_\ell^{(n)}(z) + H_\ell^{(n-1)}(z)] \qquad \text{for } n \in [0, \ell]. \tag{20}$$

We can now replace $H_\ell^{(|\bar{m}|+n)}(z_{ij})$ in (19) by its recurrence derived from (20) and then form again the $\tilde{h}_{\ell'\ell}^{ij}(|\bar{m}|)$ functions. This leads to the new equation

$$h_{\ell'\ell}^{ij}(|\bar{m}|) = \sqrt{\frac{(\ell-|\bar{m}|)(\ell-|\bar{m}|-1)}{(\ell+|\bar{m}|)(\ell+|\bar{m}|-1)}}\tilde{h}_{\ell'\ell-2}^{ij}(|\bar{m}|) - (2\ell-1)z_{ij}\sqrt{\frac{(\ell-|\bar{m}|)}{(l+|\bar{m}|)}}\tilde{h}_{\ell'\ell-1}^{ij}(|\bar{m}|)$$

$$+ (2\ell-1)z_{ij}\sqrt{\frac{(\ell'+|\bar{m}|)(\ell'-|\bar{m}|+1)}{(\ell+|\bar{m}|)(\ell+|\bar{m}|-1)}}\tilde{h}_{\ell'\ell-1}^{ij}(|\bar{m}|-1). \tag{34}$$

If now we replace $H_{\ell'}^{(n)}(z_{ij})$ by its recurrence expression in (20), we recover equation (25*a*).

Finally, we can replace both $H_\ell^{(|m|+n)}(z_{ij})$ and $H_{\ell'}^{(n)}(z_{ij})$ by their respective recurrences. We obtain then a complicated expression which can be simplified by replacing the $\tilde{h}_{\ell_2\ell_1}^{ij}(|\bar{m}|+1)$ and $\tilde{h}_{\ell_2\ell_1}^{ij}(|\bar{m}|-1)$ terms by their equivalents derived from (25*a*) and (34) respectively. This leads to our final recurrence relation

$$\tilde{h}_{\ell'\ell}^{ij}(|\bar{m}|) = a_1\tilde{h}_{\ell'\ell-2}^{ij}(|\bar{m}|) + a_2\tilde{h}_{\ell'-2\ell}^{ij}(|\bar{m}|) + a_3\tilde{h}_{\ell'\ell-1}^{ij}(|\bar{m}|) + a_4\tilde{h}_{\ell'-1\ell}^{ij}(|\bar{m}|)$$

$$+ a_5\tilde{h}_{\ell'-1\ell-2}^{ij}(|\bar{m}|) + a_6\tilde{h}_{\ell'-2\ell-1}^{ij}(|\bar{m}|) + a_7\tilde{h}_{\ell'-2\ell-2}^{ij}(|\bar{m}|) \tag{35}$$

with

$$\begin{aligned}
a_1 &= b_m(\ell)b_m(\ell-1)\\
a_2 &= (b_m(\ell')b_m(\ell'-1))^{-1}\\
a_3 &= -(2\ell-1)zb_m(\ell)\\
a_4 &= -(2\ell'-1)z/b_m(\ell')\\
a_5 &= (2\ell'-1)zb_m(\ell)b_m(\ell-1)/b_m(\ell')\\
a_6 &= (2\ell-1)zb_m(\ell)/(b_m(\ell')b_m(\ell'-1))\\
a_7 &= -b_m(\ell)b_m(\ell-1)/b_m(\ell')b_m(\ell'-1)
\end{aligned} \tag{36}$$

and

$$b_m(\ell) = \sqrt{(\ell-|\bar{m}|)/(\ell+|\bar{m}|)}. \tag{37}$$

A fast computing of the $\tilde{h}_{\ell'\ell}^{ij}(|\bar{m}|)$ can then be achieved by using (34) and (35) in the case where ℓ or $\ell' = \ell_{max}$ which would otherwise impose the calculation of a lot of unneeded terms.

5. Test

We performed our tests with the high-energy case in mind as it is for this type of calculation that the problem of speed becomes the most acute. Consequently, we did not test Chew's recurrence scheme as it is not possible to truncate the calculation. Moreover, Manar and Brouder [12] have already reported on convergence tests that show this method to be unstable at high energy.

Fritzsche's and Nozawa's methods having basically the same structure (they only differ in the way of implementing the incrementation in m), they should not differ appreciably in speed. Therefore, we only retained the latter for our tests. This left us with three methods, all of them based on the same magnetic quantum number expansion that can be truncated at high energy: Nozawa's, Rehr and Albers' and ours to which we added the direct method given by equation (9) in order to have a time reference.

We tested them in speed for the full calculation (i.e. without any truncation). For this, we computed all the values of $\tilde{g}^{ij}_{\ell'\ell}(|\vec{m}|)$ up to $\tilde{g}^{ij}_{NL-1NL-1}(NL-1)$ where NL is the maximum number of ℓ values. This was done for $r_{ij} = 2$ Å and a kinetic energy $E_k = 1000$ eV leading to $kr_{ij} = 32.4$. The results of these tests are given in table 1. These results are in units of 10^{-3} s and were obtained on an IBM RS6000 computer without any optimization. With a $-O$ optimization, the Rehr–Albers method becomes slightly faster than our method by about 30%, both of them being about three times faster than Nozawa's recursion scheme. As discussed in section 3, this result was expected as in this latter case, a lot of additional terms are necessary to the calculation. Note that this 30% difference between the Rehr–Albers method and ours occurs for NL = 20 and then decreases quickly when NL is increased.

Table 1. A comparison of the CPU time required by the different methods.

	$\delta_\ell = 5$	$\delta_\ell = 10$	$\delta_\ell = 15$	$\delta_\ell = 20$	$\delta_\ell = 25$	$\delta_\ell = 30$
Reference	6.95	67.3	305.24	8600	27 799	50 799
Nozawa	0.81	4.58	14.48	30.49	58.74	102.59
New ones	0.28	1.59	4.85	9.94	18.52	31.88
Rehr–Albers	0.48	2.14	7.63	18.06	37.40	71.78

Next we checked the stability of the methods tested. For this we kept $r_{ij} = 2$ Å and scanned the energy from 1 eV to 20 000 eV for all three methods plus the direct method where the $3j$ coefficients were calculated explicitly. We did this for NL = 5, 10, 15 and 25 and calculated $\tilde{g}^{ij}_{\ell\ell}(\ell)$ with $\ell = NL - 1$, which is the value that requires most computing and should be therefore the most subject to instability.

Only two methods, ours and the Rehr–Albers one, gave exactly the same results on the whole range of energy and for the different values of ℓ. As can be seen from figure 2, where $|\tilde{g}^{ij}_{14\,14}(14)|$ is plotted versus the energy, the Nozawa recursion scheme is unstable above 900 eV in this case. Actually, a closer look at the numerical results reveals that even at the beginning of the energy range, there are slight differences between Nozawa's method and the other ones. The limit of stability varies with NL, the Nozawa results being false over all the energy range for $|\tilde{g}^{ij}_{24\,24}(24)|$ while this limit increases to about 1450 eV for $|\tilde{g}^{ij}_{99}(9)|$. For $|\tilde{g}^{ij}_{44}(4)|$ all four methods give exactly the same results. Note that the stability limit should be sensitive to r_{ij} as well.

In order to isolate the origin of the instability of the Nozawa relations, we calculated $|\tilde{g}^{ij}_{24\,24}(m)|$ for $m = 0$, 5 and 10. When $m = 0$ or 5, we found the recurrence relations to be

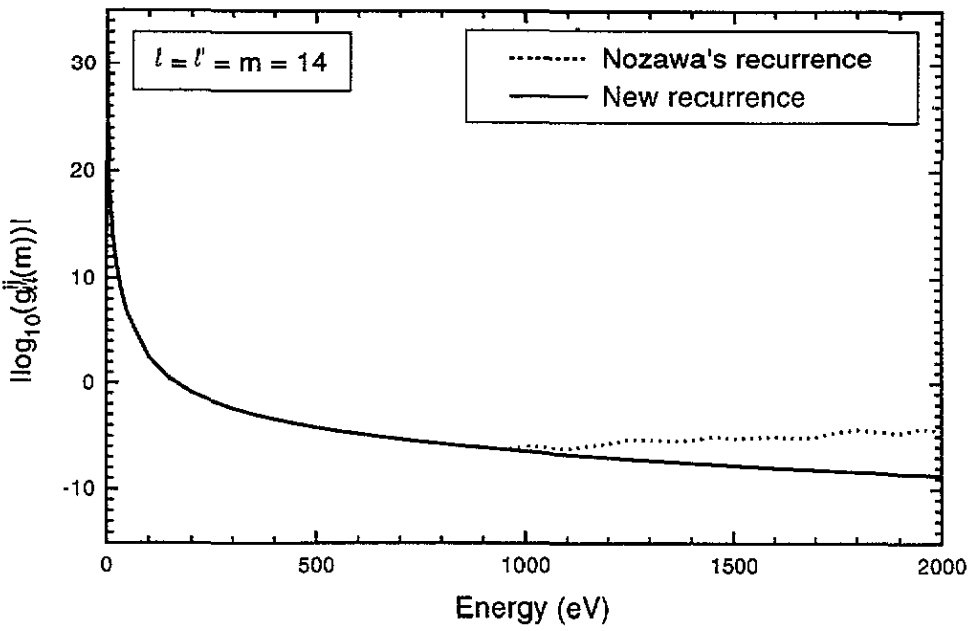

Figure 2. $|\tilde{g}^{ij}_{14\,14}(14)|$ as a function of the energy.

stable on the whole range of energy while for $m = 10$ we obtained differences in the fourth digit above 17 400 eV. This clearly means that it is the incrementation in m, equation (25*a*), that is unstable. However, this instability is not too critical as at high energy only very few values of m are necessary to achieve convergence. Note that, the instability being caused by the incrementation in m, it does not allow to draw any conclusion concerning Fritzsche's relations which do not make use of this incrementation scheme.

We found also the direct method to be unstable in certain cases. To test it, we computed $|\tilde{g}^{ij}_{24\,24}(24)|$ over the same range of energy but with r_{ij} varying from 1 Å to 5 Å by steps of 1 Å, and compared the results obtained to those obtained with the two stable methods. A difference in the fourth digit occurred at 16 000 eV for $r_{ij} = 1$ Å and down to 600 eV for $r_{ij} = 5$ Å. As the Gaunt coefficient is not affected by the path length, these results show that the recurrence relation (28) for the Hankel polynomials is not always stable. However, this instability can be easily overcome by calculating $c_\ell(kr_{ij})$ using the available stable schemes devised for $h^{(1)}_\ell(kr_{ij})$.

Then, we tested Fritzsche's statement concerning inaccuracies in the Rehr–Albers method. We performed the same kind of calculation in the range 1–20 000 eV with r_{ij} going as far down as 0.1 Å and as far up as 10 Å but did not see any instability at all. This difference in the behaviour of the Rehr–Albers method is probably due to the fact that Fritzsche tested essentially the 6×6 matrix approximation of the Rehr–Albers expansion, i.e. a low-order truncation, while we used the full expansion in our calculations.

Finally, we performed the same tests adding a small imaginary component to k and did not find any change in the stability domains.

6. Conclusion

We have derived new recurrence relations for the matrix elements of the propagator. These relations have been tested in speed and stability with other existing methods: the direct method, Nozawa's recursion scheme and the Rehr–Albers separable representation. We found our method to be both as fast and as stable as the full Rehr–Albers one while Nozawa's relations can be unstable. Furthermore, our method can be truncated at high energy without any stability problem whereas approximations in the Rehr–Albers expansion might lead to inaccuracies as discussed by Fritzsche. Finally, we found the direct method to be inaccurate at high energy or for large values of the interatomic distance due to an instability in the standard recurrence relation for the Hankel polynomials.

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