LIE GROUP CALCULATION OF THE GREEN FUNCTION OF DISORDERED SYSTEMS

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Abstract

Within the framework of the muffin-tin multiple-scattering theory, the scattering path operators are given by the inverse of a matrix consisting of atomic t-matrices and a structural matrix. The influence of the displacement of an atomic centre on the structural matrix can be described analytically using Lie group techniques. From this analytical expression and the standard perturbation expansion of the Lippmann-Schwinger equation, it is possible to write the Green function of a disordered system as a series of terms which are averages over configurations. These averages can be calculated analytically from the moments of the interatomic distances. Special terms of this series are then summed up to infinity using Dyson equation. This formalism is computationally very effective to calculate electronic properties of systems with thermal or structural disorder. In this paper, the theoretical basis of this approach is briefly described and the convergence properties of the expansions are investigated.

1 Introduction

The calculation of the electronic structure and Green function of disordered systems is known to be a very difficult problem [1]. In the field of Low Energy Electron Diffraction, Rous and coll. [2, 3] investigated, up to first order, the perturbation of the scattering matrix due to atomic displacements (see also ref.[4]). In this paper, we propose a Lie algebra approach that enables us to calculate, up to any order, the influence of atomic displacement on the system Green function. The aim of this formalism is the calculation of temperature-dependent electronic structure, and this paper describes the first steps towards this goal. We present the Lie group approach for the continuum case (positive energies), the extension to bound states being briefly discussed at the end.

2 Lie algebra of translations

The free space spherical wave functions can be displaced with a translation operator J, so that, for $\mathbf{R} = \mathbf{r} + \mathbf{r}'$

$$j_\ell(R)Y_\ell^m(\hat{R}) = \sum_{\ell' m'} j_{\ell'}(r')Y_{\ell'}^{m'}(\hat{r'})J_{\ell' m',\ell m}(\mathbf{r}) \qquad (1)$$

In their seminal paper on the matrix elements of the translation operator, Danos and Maximon [5] show that

$$J_{\ell m,\ell' m'}(\mathbf{r}) = 4\pi \sum_{\lambda\mu} i^{\ell+\lambda-\ell'} C_{\ell m \lambda\mu}^{\ell' m'}\, j_\lambda(r)Y_\lambda^\mu(\hat{r}) \qquad (2)$$

where, as usually, $j_\lambda(r)$ is a spherical Bessel function, $Y_\lambda^\mu(\hat{r})$ is a spherical harmonic and $C_{\ell m\lambda\mu}^{\ell' m'}$ is a Gaunt coefficient given, in terms of Wigner 3–j symbols, by the expression:

$$C_{\ell m\lambda\mu}^{\ell' m'} = \sqrt{\frac{(2\ell+1)(2\lambda+1)(2\ell'+1)}{4\pi}}(-1)^{m'} \begin{pmatrix} \ell & \lambda & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & \lambda & \ell' \\ m & \mu & -m' \end{pmatrix} \qquad (3)$$

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In the same paper, Danos and Maximon suggest that $J_{\ell m,\ell' m'}(\mathbf{r})$ can be written as the exponential of a matrix, in other words:

$$J_{\ell m\ell' m'}(\mathbf{r}) = \{\exp(\mathbf{A}.\mathbf{r})\}_{\ell m\ell' m'} \tag{4}$$

Lie's theorem states that $J_{\ell m,\ell' m'}(\mathbf{r})$ is the exponential of its derivative at 0. Therefore, a simple calculation [6-8] gives us the non-zero elements of the three matrices A^x, A^y and A^z.

$$A^x_{\ell' m\pm 1\ell m} = \pm\frac{1}{2}\sqrt{\frac{(\ell\pm m+1)(\ell\pm m+2)}{(2\ell+1)(2\ell+3)}}\delta_{\ell'\ell+1} \pm \frac{1}{2}\sqrt{\frac{(\ell\mp m-1)(\ell\mp m)}{(2\ell+1)(2\ell-1)}}\delta_{\ell'\ell-1} \tag{5}$$

$$A^y_{\ell' m\pm 1\ell m} = -\frac{i}{2}\sqrt{\frac{(\ell\pm m+1)(\ell\pm m+2)}{(2\ell+1)(2\ell+3)}}\delta_{\ell'\ell+1} - \frac{i}{2}\sqrt{\frac{(\ell\mp m-1)(\ell\mp m)}{(2\ell+1)(2\ell-1)}}\delta_{\ell'\ell-1} \tag{6}$$

$$A^z_{\ell' m\ell m} = -\sqrt{\frac{(\ell-m+1)(\ell+m+1)}{(2\ell+1)(2\ell+3)}}\delta_{\ell'\ell+1} + \sqrt{\frac{(\ell-m)(\ell+m)}{(2\ell+1)(2\ell-1)}}\delta_{\ell'\ell-1} \tag{7}$$

The usefulness of this expression is that the exponential of a matrix can be calculated easily with the standard series expansion. This expansion has an infinite radius of convergence and convergence is very fast when r is smaller than 2, since the norm of A^α is 1 [6]. For calculation of scattering properties of clusters and crystals, the matrix elements of the free-space Green function are needed. They can be written in terms of

$$H_{\ell m,\ell' m'}(\mathbf{r}) = -4\pi i\sum_{\lambda\mu} i^{\ell+\lambda-\ell'} C^{\ell' m'}_{\ell m\lambda\mu}\ h^+_\lambda(r)Y^\mu_\lambda(\hat{r}) \tag{8}$$

Standard arguments of Lie group theory [6] can now be used to show that, when the argument of the Green function is changed from $\mathbf{r}$ to $\mathbf{r}+\mathbf{r}'$ we can write:

$$H_{\ell m,\ell' m'}(\mathbf{r}+\mathbf{r}') = \sum_{\ell'' m''} H_{\ell m,\ell'' m''}(\mathbf{r})J_{\ell'' m'',\ell' m'}(\mathbf{r}') \tag{9}$$

The sum being convergent when $r' < r$. This is the basis of the use of Lie algebra techniques to the calculation of the electronic structure of disordered systems.

3 Application to multiple-scattering formalism

In the investigation of the scattering properties of clusters, which is a useful approach to model LEED or x-ray absorption processes, the scattering path operators τ_0^{ij} are needed [9]. They are calculated from the equation

$$\tau_0 = \left[T^{-1} - \kappa H\right]^{-1} \tag{10}$$

where the matrices have combined indices ${}_{i\ell m,j\ell' m'}$, $H^{ij}_{\ell m\ell' m'} = H_{\ell m\ell' m'}(\mathbf{R}_{ij})$, T is the atomic scattering matrix [9] and $\kappa = \sqrt{E}$. If each atomic center is now displaced from $\mathbf{R}_i$ to $\mathbf{R}_i + \mathbf{r}_i$ and the corresponding modification of $H^{ij}_{\ell m\ell' m'}$ is given by equation (9). The standard proof of Lippmann-Schwinger equation leads now to an equation giving the scattering path operator of the displaced systems in terms of that of the original system:

$$\tau = \tau_0 + \kappa\tau_0\ H\ (J-1)\ \tau \tag{11}$$

which can be expanded as a series

$$\tau = \tau_0 + \kappa\tau_0 H(J-1)\tau_0 + \kappa^2\tau_0 H(J-1)\tau_0 H(J-1)\tau_0 + \cdots \tag{12}$$

This equation is already powerful. If only the first term of this expansion is used, with J expanded up to first order, then we obtain the Tensor Leed formalism, which has proved very useful [2, 3]. However, the above expression is particularly interesting when average over configurations must be carried out, as in a thermally vibrating crystal or in an amorphous system. A straightforward extension of Fox' treatment [10] leads to an expression for the average of J over configurations

$$\langle J\rangle = \exp\left(\sum_n \frac{1}{n!}\langle(\mathbf{r}.\mathbf{A})^n\rangle\rangle_c\right) \tag{13}$$

where $\langle\rangle_c$ stands for cumulant average. This expression is valid and rapidly convergent for any distribution of configurations. In the usual case of harmonic disorder, the cumulant expansion stops at $n = 2$ and the argument of the exponential is

$$\langle r_i^\alpha r_j^\beta \rangle \left(A^\alpha A^\beta \right)_{\ell m \ell' m'} \tag{14}$$

where α and β indicate x, y or z coordinate. Further terms of expansion (12) can be averaged in the same way, using the concept of superoperators [10, 7]. For instance, up to second order, the average of Eq. (12) is.

$$\langle \tau \rangle = \tau_0 + \kappa \tau_0 H(\langle J \rangle - 1)\tau_0 + \kappa^2 \tau_0 H \langle (J-1)\tau_0(J-1) \rangle H \tau_0 + \cdots \tag{15}$$

where use was made of the fact that $HJ = JH$, which can be deduced from the commutativity of translations [6]. The advantage of this calculation scheme is that, to make the average over configurations, the calculation of τ is not required for each configuration, but only once, the influence of disorder being treated through J which can be averaged analytically. In other words, the matrix equation (10) must be solved once and the configuration averages are calculated afterwards, on much smaller matrices. This approach was used, in the simpler case of a one dimensional problem, in ref. [7]. A more accurate treatment would use a Dyson-like equation:

$$\langle \tau \rangle = \tau_0 + \tau_0 \Sigma \langle \tau \rangle \tag{16}$$

where the "self-energy" Σ can be expanded as a series

$$\Sigma = \kappa \Sigma_1 + \kappa^2 \Sigma_2 + \cdots \tag{17}$$

The classical calculation of "self-energy" in Dyson equation yields

$$\Sigma_1 = H\langle J \rangle - H \tag{18}$$

$$\Sigma_2 = H\left(\langle J \tau_0 J \rangle - \langle J \rangle \tau_0 \langle J \rangle\right) H \tag{19}$$

Up to second order, this gives us

$$\langle \tau \rangle = \left[T^{-1} - \kappa H \langle J \rangle - \kappa^2 \Sigma_2 - \cdots \right]^{-1} \tag{20}$$

Dyson equation carries out the summation of an infinity of terms from Eq. (15), however, it is computationally more demanding because it requires the inversion of a large matrix for each distribution of configurations (but not for each configuration). For instance, when calculating temperature-dependent Green function, a full inversion would be required for each temperature.

4 Asymptotic properties

In ref. [11], Butler and Zhang have made an asymptotic analysis of the various terms entering multiple-scattering equation for bound states. This type of analysis is very useful to investigate the convergence properties of the matrix equations. In this section, a similar analysis will be carried out in the case of continuum states. Using Volterra equation for the continuum wavefunction [12], it can be shown that the asymptotic expression of the scattering phase shift for large angular momentum is

$$\delta_\ell \sim \frac{-1}{4(\ell+1)(2\ell+1)} \left(\frac{e\kappa\rho}{2\ell+1} \right)^{2\ell+1} \rho^2 V(\rho) \tag{21}$$

where ρ is the muffin-tin radius and V is the spherical scattering potential. The quality of this asymptotic approximation is shown in fig. 1, where phase-shifts were calculated for a Samarium atom [13]. The asymptotic formula gives scattering phase-shifts to within a few percent, for reasonable energies, while the phase-shifts vary over 300 orders of magnitude.

For the calculation of the asymptotic form of the matrices H and $\langle J \rangle$, for large angular momentum, it is very convenient to use the contour integral definition given in ref.[5] which can be traced back to the seminal paper by Weyl [14].

$$Z_{\ell m \ell' m'}(\mathbf{R}) = \int_0^{2\pi} d\phi \int_C d(\cos\theta) Y_\ell^{m*}(\theta,\phi) \exp(i\mathbf{k}.\mathbf{R}) Y_{\ell'}^{m'}(\theta,\phi) i^{\ell-\ell'} \tag{22}$$

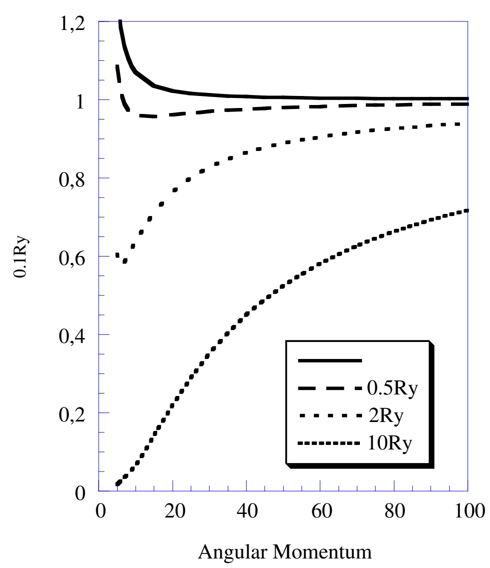

Figure 1: Ratio of exact phase-shift over asymptotic approximation for Sm.

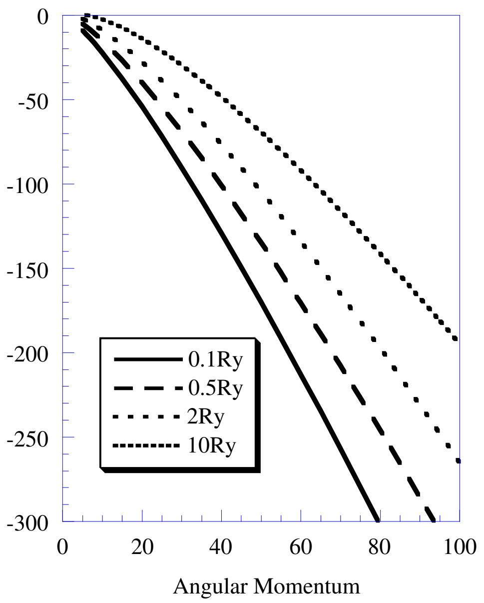

Figure 2: Decimal logarithm of phase-shift of Sm at various energies.

where

$$\exp(i\mathbf{k}.\mathbf{R}) = \exp\left[i\kappa(R^x \sin\theta\cos\phi + +R^y \sin\theta\sin\phi + R^z\cos\theta)\right] \tag{23}$$

For $Z = J$ the contour C for $\cos\theta$ goes from -1 to 1 while, for $Z = iH$ it goes from $i\infty$ to 1 via 0. Taking the special case of $\mathbf{R}$ along the z-axis, the asymptotic values of H and $\langle J\rangle$ can be calculated using multidimensional steepest-descent methods [15]. This yields, for large n

$$H_{\ell mnm'}(0,0,z) \sim -\delta_{mm'}(-1)^{\ell+m}\frac{(2\ell-1)!!}{2^\ell}\sqrt{\frac{2\ell+1}{(\ell-m)!(\ell+m)!}}\left(\frac{2n}{ez}\right)^{n+\ell+1}\frac{e^{\ell+1}}{\sqrt{n}} \tag{24}$$

Therefore, H becomes very large for large n. The quality of this asymptotic expression can be estimated from figure 3.

The convergence of $H\langle J\rangle$ in Eq. (20) can be investigated, in the case of harmonic disorder, from Eq.(13) where we take a disorder of mean square displacement $2z$ along $0z$. Then, averaging Eq.(22) over configurations and calculating the asymptotic form of $\langle J\rangle$, we obtain 0 for $n-\ell$ odd and

$$\langle J\rangle_{\ell mnm'}(0,0,z) \sim \delta_{mm'}\frac{(2\ell-1)!!}{2^\ell}\sqrt{\frac{2\ell+1}{(\ell-m)!(\ell+m)!}}\left(\frac{ez}{2n+1}\right)^{\frac{n-\ell}{2}}\frac{\sqrt{e}^{\ell+\frac{1}{2}-z}}{\sqrt{2n+1}} \tag{25}$$

for $n-\ell$ even. The main point of this calculation is to show that the product $H\langle J\rangle$ is divergent (in other words, the term $H_{\ell mnm'}\langle J\rangle_{nm'\ell'm''}$ becomes larger and larger when n increases). This divergence corresponds to the fact that, for an harmonic disorder, there is a finite probability that two atoms are at the same place, which make H divergent. This divergence must be taken into account in actual calculations, but it does not invalidate the formalism. Divergent series can be cured in many ways, one can use resummation techniques, as in ref.[16], or one can still use the asymptotic series as it is. In many cases, asymptotic series are divergent, but useful anyway (e.g. Stirling series for the factorial function [15]), because the error made in using an asymptotic series is of the order of magnitude of the smallest term in the sum. Since divergence occurs for very large values of angular momentum (n has to be much larger than κz), it is probably accurate enough to keep the first few terms in the expansion of Eq.(13). The last way to restore convergence is to use additional (quartic) cumulant moments in Eq.(13), leading to a convergent expression. This would prevent two atoms to overlap too much.

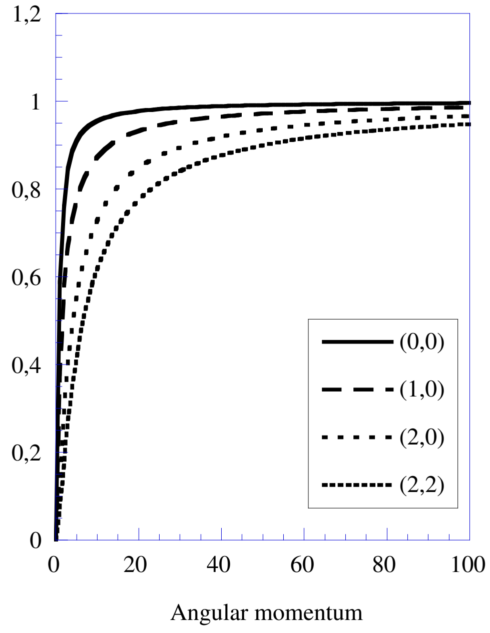

Figure 3: Asymptotic approximation over exact value for H matrix.

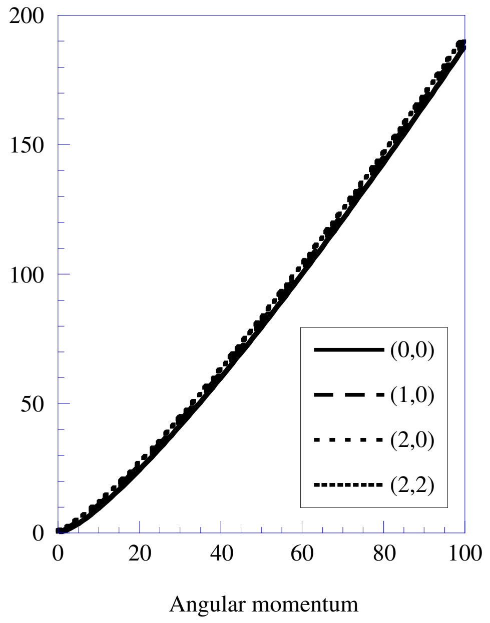

Figure 4: Decimal logarithm of $H_{\ell mnm}(1)$ for various (ℓ, m)

5 Conclusion

The Lie group approach that was presented in this paper seems promising, although practical applications were only given for a one-dimensional case [7]. However, a few extensions seem already possible. First, we did not take into account possible symmetries of the system. This can be done in a straightforward way, using normal mode of vibration of the cluster. Normal mode decomposition would also be necessary to take into account the energy transfer between the electronic system and the phonon. In the present treatment, we consider that the electron energy is not modified by vibrations, whereas energy is conserved only in the total system electrons+phonons.

A more exciting prospect would be an extension to the calculation of bound states, leading to an easy computation of temperature-dependent electronic structure. Most of the steps of the present paper can be adapted straightforwardly to the case when κ^2 is negative. The problem is that Eq.(10) would be constrained by the condition that the corresponding determinant be zero. Therefore, one should consider the perturbation of the determinant for a small variation of the matrix elements. This problem is delicate, although manageable.

A last extension would be to investigate the change of the scattering path operators when the energy (κ) is modified. In that case Eq.(9) becomes

$$H(\kappa\mathbf{r} + \delta\kappa\mathbf{r}) = H(\kappa\mathbf{r})J(\delta\kappa\mathbf{r}) \tag{26}$$

Therefore, once the change in T is also taken into account, it is possible to know the Green function at an energy from the value it has at a nearby energy. This yields, for instance, a differential equation for the scattering path operator:

$$\frac{d\tau^{ij}}{d\kappa} = \sum_{kl} \tau^{ik} \left[H^{kl} \left(1 + \kappa \mathbf{R}_{kl}.\mathbf{A}\right) - \frac{d}{d\kappa}\left(T^{-1}\right)^{kl} \right] \tau^{lj} \tag{27}$$

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