

SCATTERING PATH FORMALISM FOR THE PROPAGATION OF INTERACTING COMPOUNDS IN ORDERED AND DISORDERED MATERIALS

J. BERAKDAR*

*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2,
06120 Halle, Germany*

Received 15 February 2000

This study presents a theoretical framework for the propagation of a compound consisting of N interacting particles in a multicenter potential. A novel Green operator approach is proposed that disentangles the geometrical and dynamical properties of the scatterers from the internal evolution of the projectile compound. Furthermore, the transition operator for the scattering from the multicenter potential is expanded in terms of many-body scattering path operators, which in turn are expressed in terms of single site transition operators that are amenable to computations. To deduce the correlated many-body Green operator of the scattering compound, a cumulative method is designed that reduces the problem to the evaluation of Green operators of systems with a reduced number of interacting particles. This is particularly useful for efficient calculations and encompasses the usual perturbative approaches.

When an electronic system is subjected to an external perturbation, it may respond collectively by the emission of electrons. A variety of important structural and electronic properties of materials can then be deduced by analyzing the spectrum of the emitted electron flux. Prominent examples of such analytical techniques are electron energy loss spectroscopy,¹ the (low, high and medium energy) electron diffraction method² and single photoemission measurements.³ Correspondingly, a number of reliable theoretical concepts have been put forward to deal with the single particle scattering from ordered and disordered matter.^{4,5}

On the other hand, the propagation of a many-body system with coupled internal degrees of freedom through a multicenter potential is much less understood theoretically. Examples of such cases are the scattering of atoms, molecules and correlated electrons from surfaces (see Ref. 6 and references therein). A detailed analysis of such processes is, however, of great fundamental and technological

importance, as a number of important catalytic reactions occur at surfaces.⁷

The difficulties in the theoretical treatment stem from the nonseparability introduced by the correlated many-body scattering compound and the subtle coupling of the internal motion (of the constituents of the compound) to the external multicenter potential.

This work aims at developing a systematic framework for the description of a compound with a finite number of interacting particles that propagates in the field created by a multicenter potential. This potential could be ordered or disordered, but it should be possible to cast it reasonably well in a nonoverlapping muffin tin form.

The fundamental quantity that describes the behavior of the correlated system in the presence of the external potential is the total Green operator \mathcal{G} , which is the resolvent of the respective Hamiltonian. Our goal is thus to find exact expressions for \mathcal{G} in terms of single particle quantities that are

*E-mail: jber.mpi-halle.de

computationally accessible. Our strategy is to decouple formally the degrees of freedom of the compound with N interacting particles from the external scattering potential. For the Green operator of the N -body system we propose an incremental method due to which the Green operator is cumulatively reduced to Green operators of systems with a reduced number of interactions. This procedure can be successively repeated until a reduced interacting system is reached whose Green operator is known. In a second step the scattering compound is considered as a quasi-single-particle with an internal dynamical structure. For the scattering of this quasiparticle we design a scattering path operator formalism that expresses the multisite many-body transition operator in terms of single site transition operators.

For a mathematical formulation we consider a nonrelativistic compound consisting of N correlated particles. The total interaction within this system is assumed to be described by a potential of the form $U_{\text{int}}^{(N)} = \sum_{j>i=1}^N v_{ij}$, where v_{ij} have not been further specified at this stage. This structured projectile is then scattered from an external multicenter potential W_{ext} which can be cast in terms of a superposition of M individual nonoverlapping potentials, w_i , acting within specific distinguishable domains Ω_i , i.e. $W_{\text{ext}} = \sum_i^M w_i$, $\Omega_i \cap \Omega_j = 0$, $\forall j \neq i$. Thus, the correlated system is coupled to the external scattering potential via

$$W_{\text{ext}} = \sum_k^M \sum_l^N w_{kl}, \quad (1)$$

where w_{kl} is the interaction of particle l with the scattering site k . The total Hamiltonian of the system can be written as $\mathcal{H} = H_{\text{int}}^{(N)} + W_{\text{ext}}$, where $H_{\text{int}}^{(N)} = K + U_{\text{int}}^{(N)}$, and K being the kinetic energy operator. The behavior of the correlated system, characterized by $H_{\text{int}}^{(N)}$, when subjected to the external potential W_{ext} is described by the total Green operator (the resolvent of \mathcal{H}) which satisfies the relation

$$\mathcal{G} = G_{\text{int}}^{(N)} + G_{\text{int}}^{(N)} T_{\text{ext}} G_{\text{int}}^{(N)}, \quad (2)$$

$$T_{\text{ext}} = W_{\text{ext}} + G_{\text{int}}^{(N)} W_{\text{ext}} T_{\text{ext}}. \quad (3)$$

Here T_{ext} is the so-called transition operator and $G_{\text{int}}^{(N)}$ is the Green operator of the correlated system when the external potential is switched off. From

Eqs. (2) and (3) it is clear that \mathcal{G} can be formulated as $\mathcal{G} = AB$, where $A = \mathbf{1} + G_{\text{int}}^{(N)} T_{\text{ext}} = \mathbf{1} + G_{\text{int}}^{(N)} W_{\text{ext}} + G_{\text{int}}^{(N)} W_{\text{ext}} G_{\text{int}}^{(N)} W_{\text{ext}} + \dots$ and $B = G_{\text{int}}^{(N)}$. These relations for \mathcal{G} disentangle the internal degrees of freedom of the projectile, described by B , from the dynamical and geometrical properties of the external potential scattering that are described by A . The external motion is coupled to the internal one via $G_{\text{int}}^{(N)}$, which occurs in the expression for A . Thus, the task is focused on finding simple and mathematically sound expressions for $G_{\text{int}}^{(N)}$ and T_{ext} .

The total internal potential $U_{\text{int}}^{(N)}$ is decomposed as

$$U_{\text{int}}^{(N)} = \sum_{j=1}^N u_j^{(N-1)}, \quad (4)$$

$$u_j^{(N-1)} = \sum_{k=1}^{N-1} u_k^{(N-2)}, \quad j \notin [1, N-1], \quad (5)$$

where $u_j^{(N-1)} = \tilde{u}_j^{(N-1)} / (N-2)$, with $\tilde{u}_j^{(N-1)}$ being the total potential of the correlated systems when $N-1$ particles are interacting while particle j is free. In Fig. 1 the expansion (4) is explained geometrically.

Let us introduce the Green operator $G_M^{(N-1)}$ of a system with the total potential $\sum_{j=1}^M u_j^{(N-1)}$, $M \in [1, N]$ (note that $G_N^{(N-1)} \equiv G_{\text{int}}^{(N)}$). As $H_{\text{int}}^{(N)} = (K + \sum_{j=1}^{M-1} u_j^{(N-1)}) + \sum_{j=M}^N u_j^{(N-1)}$, we can treat $G_{M-1}^{(N-1)}$ as the reference (known) Green operator and deduce from the Lippmann–Schwinger equation the recurrence relations

$$G_{\text{int}}^{(N)} = G_{N-1}^{(N-1)} [\mathbf{1} + u_N^{(N-1)} G_N^{(N-1)}] \quad (6)$$

$$G_{N-1}^{(N-1)} = G_{N-2}^{(N-1)} [\mathbf{1} + u_{N-1}^{(N-1)} G_{N-1}^{(N-1)}]. \quad (7)$$

These equations are reformulated in the simple but exact relation

$$G_{\text{int}}^{(N)} = G_0^{-N+1} \prod_{j=1}^N [G_0 + G_0 u_j^{(N-1)} G_j^{(N-1)}]. \quad (8)$$

The physical meaning of the operators $G_j^{(N-1)}$ which determine the expansion (8) is readily seen from Fig. 2 for a compound with six interacting constituents. It is clear from this diagram for the six-particle system that each of the reduced five-particle diagrams can be further expanded in terms of four-particle diagrams. To reach a simplified expression we note that $\sum_{i=1}^j u_i^{(N-1)} =$

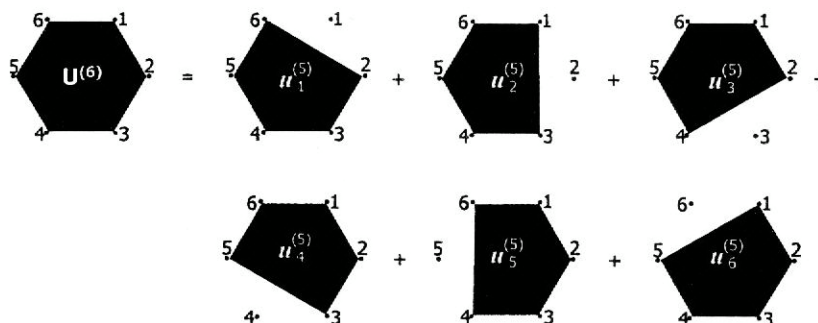


Fig. 1. Pictorial geometric sketch of the total potential expansion (4) for six interacting particles. The particles are enumerated and marked by the full dots at the corners of the hexagon. The hexagon stands for the full potential $U^{(6)}$ of the six correlated particles. According to Eq. (4), the hexagon can be broken down into six pentagons. Each pentagon symbolizes the full five-body potential $u_j^{(5)}$ of those five particles situated at the corners of the pentagon, whereas the particle not at a corner (particle j) is free.

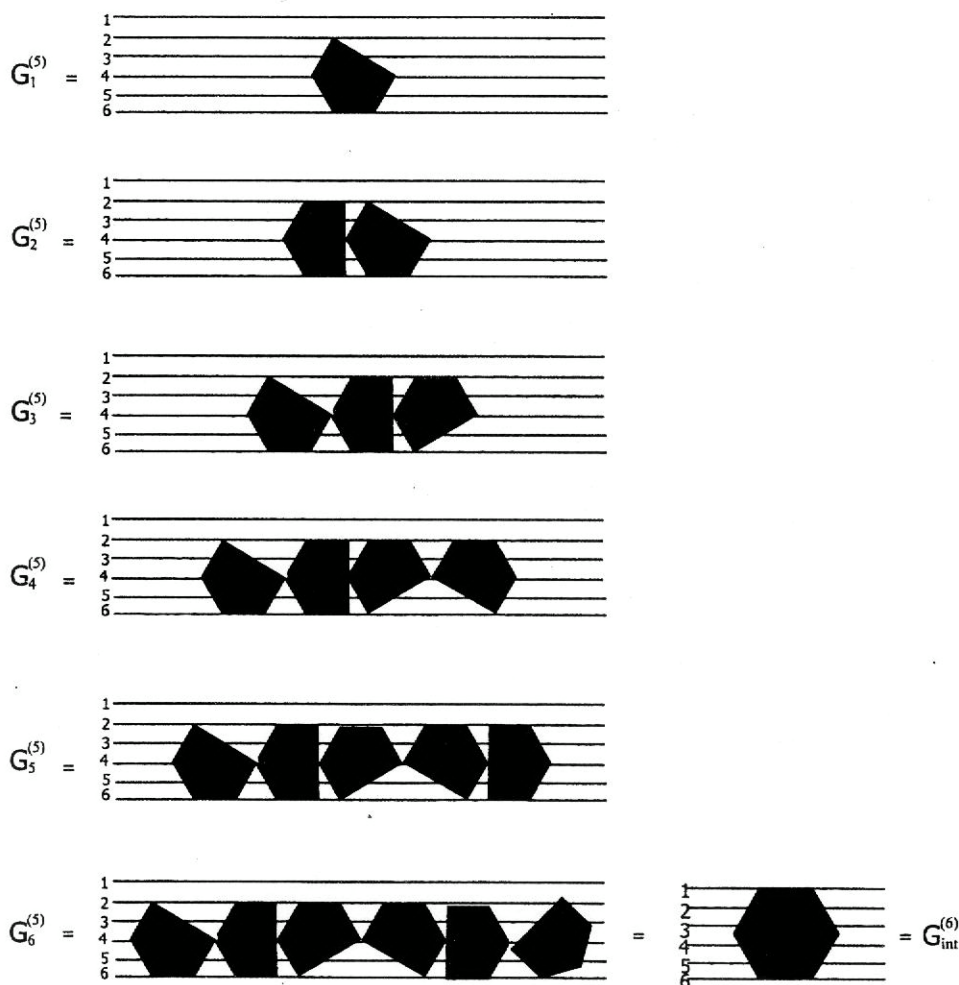


Fig. 2. The Green operators $G_j^{(N-1)}$ which occur in the expansion (6) are illustrated diagrammatically. As in Fig. 1, we choose an example of six interacting particles. The hexagons and the oriented pentagons stand for the same potentials, as explained in Fig. 1. The particles are indicated by straight lines. The interaction that occurs in each Green operator is the sum of the pentagons depicted in the respective diagrams. Only particles that cross a pentagon or a hexagon are interacting.

$u_j^{(N-1)} + \sum_{i=1}^{j-1} u_i^{(N-1)}$. Therefore, the Green operator $G_j^{(N-1)}$ satisfies the equation $G_j^{(N-1)} = g_j^{(N-1)} + g_j^{(N-1)} [\sum_{k=1}^{j-1} u_k^{(N-1)}] G_j^{(N-1)}$, where $g_j^{(N-1)}$ is the Green operator involving the interaction $u_j^{(N-1)}$ only. Inserting this relation into Eq. (8), we deduce that the leading term of the expansion (8) is given by the recurrence relations

$$G_{\text{int}}^{(N)} = G_0^{-N+1} \prod_{j=1}^N \left\{ G_0 + G_0 u_j^{(N-1)} g_j^{(N-1)} + G_0 u_j^{(N-1)} g_j^{(N-1)} \times \left[\sum_{k=1}^{j-1} u_k^{(N-1)} \right] G_j^{(N-1)} \right\}, \quad (9)$$

$$G_{\text{int}}^{(N)} \stackrel{1.\text{order}}{=} G_0^{-N+1} \prod_{j=1}^N g_j^{(N-1)} \quad (9)$$

$$g_j^{(N-1)} \stackrel{1.\text{order}}{=} G_0^{-N+2} \prod_{l=1}^{N-1} g_l^{(N-2)}, \quad j \notin [1, N-1]. \quad (10)$$

In other words, the Green operator of an N -body system is, in a first order approximation, a product of N Green operators of all the different interacting $N-1$ subsystems that can be combined within the N -body system. The Green operators of the $N-1$ subsystems can in turn be reduced in the same manner to a product of those of the $(N-2)$ -body subsystems that exist in the $(N-1)$ -particle system. Figure 3 gives a diagrammatic representation of this hierarchical procedure. In practice, one starts the incremental method as depicted in Fig. 3 from a system with a reduced number of interacting particles M for which the Green operator is known. Then, the recipe given above yields the solution (the Green operator) when $M+1$ particles are interacting. This procedure has to be further continued to reach the interacting N -body system. It is important to realize that this approach is not perturbative and that all interactions are treated on an equal footing. On the other hand, a perturbative treatment is encompassed in the expansion (9) through the Born series for $g_j^{(k)}$, $j, k \in [1, N]$.

Having established a reduction formula for the many-body Green operator, we turn now to dealing with the transition operator T_{ext} , as defined by

Eq. (3). The aim is to express it in terms of single site transition operators. For this purpose we introduce $w^{(k)} := \sum_l^N w_{kl}$ as the interaction of all N interacting particles with the site k . The external potential (1) reads $W_{\text{ext}} = \sum_{k=1}^M w^{(k)}$. Thus, T_{ext} can be expanded in a sum as

$$T_{\text{ext}} = \sum_{k=1}^M q^{(k)} \quad (11)$$

$$q^{(k)} = w^{(k)} + w^{(k)} G_{\text{int}}^{(N)} T_{\text{ext}} \quad (12)$$

$$q^{(k)} = w^{(k)} + w^{(k)} G_{\text{int}}^{(N)} q^{(k)} + \sum_{l \neq k}^M w^{(k)} G_{\text{int}}^{(N)} q^{(l)}. \quad (13)$$

Now we introduce the k site transition operator of the correlated compound as $t_k = w^{(k)} + w^{(k)} G_{\text{int}}^{(N)} t_k$ and rewrite Eq. (13) as

$$q^{(k)} = t_k + \sum_{l \neq k}^M t_k G_{\text{int}}^{(N)} q^{(l)}. \quad (14)$$

Combining this relation with Eq. (11) leads to

$$T_{\text{ext}} = \sum_k^M t_k + \sum_{l \neq k}^M t_k G_{\text{int}}^{(N)} (t_l + w_l G_{\text{int}}^{(N)} T_{\text{ext}}). \quad (15)$$

Following the treatment by Gyorffy^{8,9} of the single particle scattering from a multicenter potential, we introduce the *many-body scattering path operators*, τ^{ij} , as

$$\tau^{ij} = t_i \delta_{ij} + \sum_{k \neq i}^M t_i G_{\text{int}}^{(N)} \tau^{ik} = t_i \delta_{ij} + \sum_{k \neq j}^M \tau^{ik} G_{\text{int}}^{(N)} t_j \quad (16)$$

and sum over j . The comparison with Eq. (14) yields $q^{(i)} = \sum_j^M \tau^{ij}$, and from Eq. (11) we finally conclude that

$$T_{\text{ext}} = \sum_i^M q^{(i)} = \sum_{ij}^M \tau^{ij}. \quad (17)$$

The physical interpretation of t_k , $q^{(k)}$ and τ^{ij} is as follows. The operator t_k describes the scattering of the correlated system ($H_{\text{int}}^{(N)}$) as a whole from the site k in the absence of all the other scatterers, whereas $q^{(k)}$ characterizes the collision of this correlated system from the site k in the presence of all other scattering centers. The operators τ^{kl} describe the transition of the correlated projectile under the action

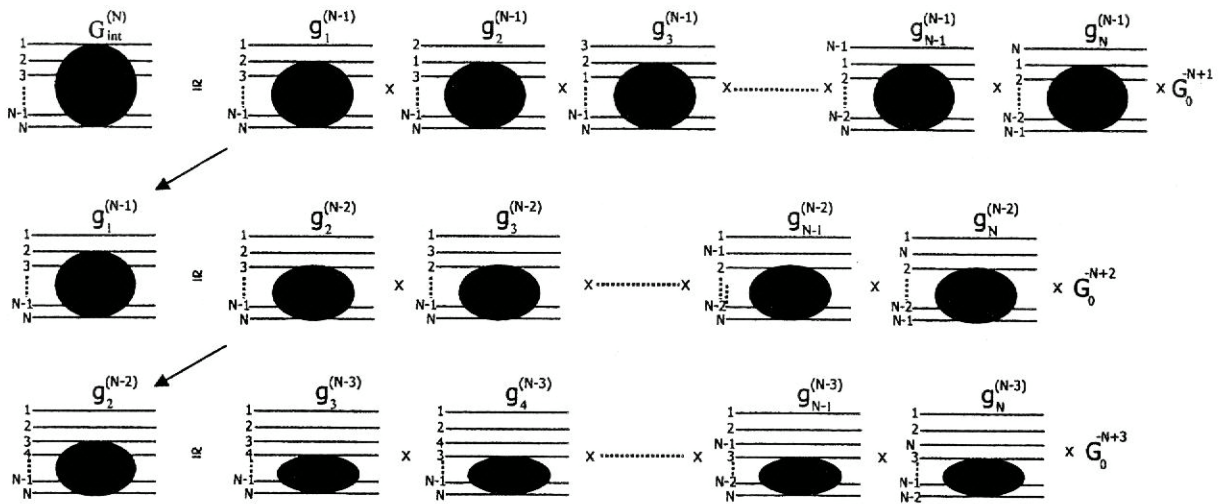


Fig. 3. Schematic representation of the approximation (9), (10) for N interacting particles. The total potential is labeled by the black circle and the $N - 1$, $N - 2$ and $N - 3$ body potentials are indicated by ellipses with different eccentricities. The particles are shown by the solid lines. Only those particles that cross an ellipse are interacting. Each diagram stands for the Green operator (shown in the diagram) of a system with the potential symbolized by the circles and/or the ellipses.

of w_k following an initial scattering from the potential centered around the site l . Thus, the transition operator from the multicenter potential T_{ext} is broken down into successive single site transitions that are computationally more accessible. Combining Eqs. (17) and (8) we arrive at the final exact expression for the total Green operator (2):

$$\mathcal{G} = \left[1 + G_{\text{int}}^{(N)} \sum_{ij}^M \tau^{ij} \right] G_0^{-N+1} \times \prod_{k=1}^N [G_0 + G_0 u_j^{(N-1)} G_k^{(N-1)}]. \quad (18)$$

As evident from Eqs. (10) and (16), the components of the main expression (18) can be obtained from established single particle theories. The first order term of the exact expansion (18) is

$$\mathcal{G} \approx \left[1 + G_0 \sum_{ij}^M \tau^{ij} \right] G_0^{-N+1} \prod_{j=1}^N g_j^{(N-1)}. \quad (19)$$

In conclusion, we have proposed a nonperturbative scheme for the theoretical treatment of correlated many-body finite systems from a multicenter potential. The total Green operator is reduced to the evaluation of Green operators of systems with a reduced

number of interactions and to the sequential scattering of these reduced systems as a whole from a single site. This has been achieved by the development of an incremental method that yields the Green operator of a system with N interactions from that for systems involving $N-l$ interactions, where $l \in [1, N-2]$. For the scattering from the external potential we designed a many-body scattering path formalism that relates the multicenter transition operator to single site transition operators.

References

1. H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, London, 1982).
2. M. A. van Hove, W. H. Weinberg and C.-M. Chan, *Low Energy Electron Diffraction*, Springer Series in Surface Science (Springer, Berlin, 1986).
3. S. Hüfner, *Photoelectron Spectroscopy*, No. 82, Springer Series in Solid-State Science (Springer-Verlag, Berlin, 1995).
4. I. Turek, V. Drchal, J. Kudrnovský, M. Šob and P. Weinberger, *Electronic Structure of Disordered Alloys, Surfaces, and Interfaces* (Kluwer, Boston, London, Dordrecht, 1997).
5. P. Weinberger, *Electron Scattering Theory for Ordered and Disordered Matter* (Clarendon, Oxford, 1990).
6. V. Bortolani, N. H. March and M. P. Tosi (eds.),

- Interaction of Atoms and Molecules with Solid Surfaces* (Plenum, New York, 1990).
7. D. A. King and D. P. Woodruff (eds.), *Chemical Physics of Solid Surfaces and Heterogeneous Catalysis* Vol. 3, *Chemisorption Systems, Part A* (Elsevier, Amsterdam, 1990).
 8. B. L. Gyorffy, *Fondamenti di fisica dello stato solido, Scuola Nazionale di Struttura della Materia* (1971).
 9. B. L. Gyorffy and M. J. Stott, in: D. J. Fabian and L. M. Watson (eds.), *Bandstructure Spectroscopy of Metals and Alloys* (Academic, London, 1973).