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# The Green function of degenerate systems

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A rigorous non perturbative adiabatic approximation of the evolution operator in the many-body physics of degenerate systems is derived. This approximation is used to solve the long-standing problem of the choice of the initial states of  $H_0$  leading to eigenstates of  $H_0 + V$  for degenerate systems. These initial states are eigenstates of  $P_0 V P_0$ , where  $P_0$  is the projection onto a degenerate eigenspace of  $H_0$ . This result is used to give the proper definition of the Green function, the statistical Green function and the non-equilibrium Green function of degenerate systems. The convergence of these Green functions is established.

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Non-perturbative Green function methods, such as the GW approximation [1] or the Bethe-Salpeter equation [2, 3], have brought remarkable progress in the calculation of the electronic structure and dielectric response of semiconductors. The extension of these methods to transition metal systems faces a serious difficulty: the standard Green function can only be defined when the initial state  $|0\rangle$  of the system without interaction is a single Slater determinant. In physical terms, each single-particle orbital or Bloch state has to be either occupied or unoccupied at zero temperature. However, the physics of transition metal often contradicts this requirement. For the example of a  $V^{3+}$  ion in an octahedral environment, we do not know a priori how the two  $3d$  electrons are distributed over the three degenerate  $t_{2g}$  orbitals.

More generally, for a system described by a Hamiltonian  $H = H_0 + V$  where the ground state of  $H_0$  is degenerate, we need to know how to determine the *parent states*, i.e. the initial states of  $H_0$  that evolve into eigenstates of  $H$  by adiabatically switching the interaction.

This problem has been discussed for a long time in chemical physics [4, 5], nuclear physics [6, 7], atomic physics [8, 9] and solid state physics [10]. Esterling and Lange [10] summarized the situation as follows: “Since  $H_0$  has degenerate ground states, the choice of the state  $|0\rangle$  must be made with care, and this may be considered the key to the problem.” This question is important because, as we shall see, the parent state is the vector  $|0\rangle$  that must be used in the formula defining the Green function. It is often thought that the interacting Hamiltonian must first be solved before determining the parent states. We show here that this is not the case.

In the present paper, we carry out a non-perturbative analysis of the adiabatic evolution of a degenerate system and we determine the exact form of its singularities. This enables us to derive: (i) an easy and explicit method to determine the parent states; (ii) a non-perturbative

proof that the Gell-Mann and Low formula generally converges only for these parent states; (iii) the formula for the Green function of degenerate systems; (iv) the range of validity of the so-called *statistical* Green function; (v) the singularity structure of the non-equilibrium Green function of degenerate systems.

*Adiabatic switching.* Many-body theory [11, 12] is usually based on the adiabatic switching of the interaction, i.e. the transformation of the time-independent Hamiltonian  $H = H_0 + V$  into the time-dependent one  $H_0 + e^{-\varepsilon|t|}V$ . Adiabatic switching turns the non degenerate ground state  $|0\rangle$  of  $H_0$  into an eigenstate  $|\Psi_{\text{GML}}\rangle$  of  $H$  first proposed by Gell-Mann and Low [13] in 1951

$$|\Psi_{\text{GML}}\rangle = \lim_{\varepsilon \rightarrow 0} \frac{U_\varepsilon(0, -\infty)|0\rangle}{\langle 0|U_\varepsilon(0, -\infty)|0\rangle}, \quad (1)$$

where the evolution operator  $U_\varepsilon(t, t')$  is the solution of

$$i \frac{\partial U_\varepsilon(t, t')}{\partial t} = e^{iH_0 t} e^{-\varepsilon|t|} V e^{-iH_0 t} U_\varepsilon(t, t'),$$

with the initial condition  $U_\varepsilon(t', t') = 1$ . The wavefunction  $|\Psi_{\text{GML}}\rangle$  is then used to build the Green function of the system [11, 12]. However, Gell-Mann and Low did not prove that the limit of eq. (1) exists [12]. The convergence of  $|\Psi_{\text{GML}}\rangle$  for nondegenerate systems was rigorously proved by Nenciu and Rasche in 1989 [14].

For a degenerate ground state  $|0\rangle$  of  $H_0$ , the Gell-Mann and Low formula generally fails to converge when  $\varepsilon \rightarrow 0$ , as can be seen even for a trivial two-level system [15]. In the following, we use recent advances in the mathematical analysis of the adiabatic approximation (see [16] for a review) to extend the Gell-Mann and Low formula to degenerate systems.

*Adiabatic approximation.* We consider a Hamiltonian  $H(s) = H_0 + e^s V$ . The eigenvalues of  $H(s)$  are denoted by  $E_j(s)$  and its eigenprojectors by  $P_j(s)$ . We recall that, if the eigenvalue  $E_j(s)$  is  $n_j$ -fold degenerate, the

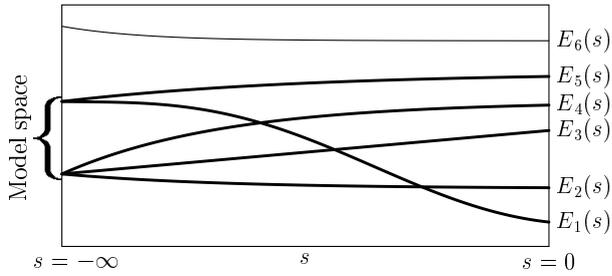


FIG. 1: Example of allowed eigenvalue pattern

eigenprojector is  $P_j(s) = \sum_{k=1}^{n_j} |\varphi_{jk}(s)\rangle\langle\varphi_{jk}(s)|$ , where  $\{|\varphi_{jk}(s)\rangle\}$  is a set of  $n_j$  orthonormal eigenstates of  $H(s)$  for the eigenvalue  $E_j(s)$ . The *model space*  $M$  is the vector space generated by the eigenstates corresponding to  $N_0$  eigenvalues of  $H_0 = H(-\infty)$ . Each eigenvalue can be degenerate and is possibly split by the perturbation  $V$ , so that the  $N_0$  eigenvalues of  $H_0$  become  $N$  eigenvalues  $E_1(s), \dots, E_N(s)$  of  $H(s)$ , with  $N \geq N_0$ , see fig. 1.

Again, each  $E_j(s)$  can be degenerate. As a first hypothesis, we assume that the  $N$  eigenvalues  $E_j(s)$  are separated by a finite gap from the rest of the spectrum of  $H(s)$ . The eigenvalues of the model space are allowed to cross. Our second hypothesis is that the perturbation  $V$  is small, in a certain sense [17]. This assumption is satisfied in most cases of practical interest. In particular, it holds for a Hamiltonian describing the many-body Coulomb interaction of electrons and nuclei [18]. As a consequence, we can choose eigenvalues, eigenstates and eigenprojectors that are analytic functions of  $s$  [18].

The adiabatic approximation is built according to Kato's method [18]. We define  $P_{N+1}(s) = 1 - \sum_{j=1}^N P_j(s)$  and the antisymmetric operator

$$K(s) = - \sum_{j=1}^{N+1} P_j(s) \frac{dP_j(s)}{ds}.$$

The *intertwiner*  $A(s, s_0)$  is the solution of  $dA(s, s_0)/ds = K(s)A(s, s_0)$ , with the boundary condition  $A(s_0, s_0) = 1$ . The intertwiner is a unitary operator that satisfies the intertwining property:  $A(s, s_0)P_j(s_0) = P_j(s)A(s, s_0)$ . For notational convenience, we denote  $P_j(-\infty)$  by  $P_j^0$  in the rest of the paper. We define a phase operator  $\Phi_\varepsilon$  projected onto the  $N$  eigenspaces by  $\Phi_\varepsilon P_j^0 = e^{i\theta_j/\varepsilon} P_j^0$ , where  $\theta_j = - \int_{-\infty}^0 (E_j(s) - E_j(-\infty)) ds$ . Finally, we define the adiabatic evolution operator by  $U_\varepsilon^A(0, -\infty) = A(0, -\infty)\Phi_\varepsilon$ . Our most useful mathematical results are: (i)  $A(0, -\infty)$  is well defined, (ii)  $\Phi_\varepsilon$  and  $U_\varepsilon^A(0, -\infty)$  are well defined for any  $\varepsilon > 0$ , (iii)  $U_\varepsilon^A(0, -\infty)P_j^0$  approximates the evolution operator  $U_\varepsilon(0, -\infty)P_j^0$ :

$$\lim_{\varepsilon \rightarrow 0} \|U_\varepsilon^A(0, -\infty)P_j^0 - U_\varepsilon(0, -\infty)P_j^0\| = 0.$$

The main consequence of these statements is that the divergence of the evolution operator is entirely described by

the phase operator. The proof of these results (especially (iii)) is fairly technical and is deferred to our companion mathematical paper [19].

*Construction of the parent states.* We give now an explicit way to determine the projections  $P_j^0$ , from which the parent states can be defined.

For notational convenience, we denote  $e^s$  by  $\lambda$  and the eigenvalues and eigenprojections are written in terms of  $\lambda$ . We denote by  $\bar{E}_j(\lambda)$  and  $|\bar{\varphi}_{jk}(\lambda)\rangle$  the eigenvalues and eigenstates of  $H_0 + \lambda V$ . They can be expanded as [19]

$$\bar{E}_j(\lambda) = \sum_{n=0}^{\infty} \lambda^n E_j^n, \quad |\bar{\varphi}_{jk}(\lambda)\rangle = \sum_{n=0}^{\infty} \lambda^n |\varphi_{jk}^n\rangle,$$

with the normalization  $\langle\varphi_{jk}^0|\bar{\varphi}_{jk}(\lambda)\rangle = 1$ . The eigenstates  $|\bar{\varphi}_{jk}(\lambda)\rangle$  are assumed orthonormal only at  $\lambda = 0$ , where  $P_j^0 = \sum_{k=1}^{n_j} |\varphi_{jk}^0\rangle\langle\varphi_{jk}^0|$ .

The Schrödinger equation  $(H_0 + \lambda V)|\varphi_{jk}(\lambda)\rangle = E_j(\lambda)|\varphi_{jk}(\lambda)\rangle$ , gives, to order 0,  $H_0|\varphi_{jk}^0\rangle = E_j^0|\varphi_{jk}^0\rangle$ , so that  $|\varphi_{jk}^0\rangle$  is an eigenstate of  $H_0$  with energy  $E_j^0$ . We assume that  $E_j^0$  is one of the  $N_0$  eigenvalues of the model space, so that  $|\varphi_{jk}^0\rangle$  belongs to the model space. However, the degeneracy of  $E_j^0$  as an eigenvalue of  $H_0$  is generally larger than the degeneracy of  $E_j(\lambda)$ . Therefore, we need more information to determine the  $n_j$  states  $|\varphi_{jk}^0\rangle$ . The Schrödinger equation to order  $\lambda$  gives us  $(H_0 - E_j^0)|\varphi_{jk}^1\rangle = (E_j^1 - V)|\varphi_{jk}^0\rangle$ . This equation can only have a solution if  $\langle\psi_m^0|(E_j^1 - V)|\varphi_{jk}^0\rangle = 0$ , where  $\{|\psi_m^0\rangle\}$  is a complete set of eigenstates of  $H_0$  with energy  $E_j^0$ . Therefore, the initial states  $|\varphi_{jk}^0\rangle$  are eigenstates of  $H_0$  with energy  $E_j^0$  and eigenstates of  $P_{E_j^0} V P_{E_j^0}$  with eigenvalue  $E_j^1$ , where  $P_{E_j^0}$  is the projection onto the eigenspace of  $H_0$  with eigenvalue  $E_j^0$ . In general, the degeneracy is split at this order, in the sense that there are only  $n_j$  states that are simultaneously eigenstates of  $H_0$  with energy  $E_j^0$  and of  $P_{E_j^0} V P_{E_j^0}$  with eigenvalue  $E_j^1$ . Otherwise, for instance when  $P_{E_j^0} V P_{E_j^0}$  is zero by symmetry, the equations coming from higher powers of  $\lambda$  must be taken into account to determine  $|\varphi_{jk}^0\rangle$ . Standard methods exist [20] to calculate this higher-order splitting.

We usually have no a priori knowledge of  $n_j$  and  $E_j^1$ . However, we can calculate all the eigenstates of  $H_0$  and, for each energy  $E_j^0$ , we can diagonalize  $P_{E_j^0} V P_{E_j^0}$ . This is an easy task because the dimension of the model space is small. Then, each state must be examined to see if it cannot be further split by higher order terms. When degeneracy is due to the symmetry of the Hamiltonian  $H(s)$ , this can be deduced from the dimension of the irreducible representations to which the states belong.

We have thus constructed  $|\varphi_{jk}^0\rangle$  from which we can build  $P_j^0$ . Now, a *parent state* is defined as a state  $|\phi\rangle$  such that, for some  $j$ ,

$$P_j^0|\phi\rangle = |\phi\rangle. \quad (2)$$

*Generalized Gell-Mann and Low wavefunction.* We show that the parent states previously defined lead to convergent Gell-Mann and Low wavefunctions. For a parent state  $|\phi_j\rangle$  such that  $P_j^0|\phi_j\rangle = |\phi_j\rangle$ , the adiabatic approximation enables us to approximate  $U_\varepsilon(0, -\infty)|\phi_j\rangle$  with  $U_\varepsilon^A(0, -\infty)|\phi_j\rangle$ . We have from eq. (2)

$$U_\varepsilon^A(0, -\infty)|\phi_j\rangle = e^{i\theta_j/\varepsilon}A(0, -\infty)|\phi_j\rangle.$$

Therefore, the following limit exists:

$$\begin{aligned} |\Psi_{\text{GML}}\rangle &= \lim_{\varepsilon \rightarrow 0} \frac{U_\varepsilon(0, -\infty)|\phi_j\rangle}{\langle \phi_j | U_\varepsilon(0, -\infty) | \phi_j \rangle} \\ &= \frac{A(0, -\infty)|\phi_j\rangle}{\langle \phi_j | A(0, -\infty) | \phi_j \rangle}. \end{aligned}$$

The Gell-Mann and Low wavefunction  $|\Psi_{\text{GML}}\rangle$  is indeed an eigenstate of  $H_0 + V$  with energy  $E_j(0)$  because  $P_j(0)|\Psi_{\text{GML}}\rangle = |\Psi_{\text{GML}}\rangle$ . To show this, we use the intertwining property of  $A(0, -\infty)$ :

$$\begin{aligned} P_j(0)A(0, -\infty)|\phi_j\rangle &= A(0, -\infty)P_j^0|\phi_j\rangle \\ &= A(0, -\infty)|\phi_j\rangle. \end{aligned}$$

In practice, we are interested in the Gell-Mann and Low wavefunction that is the ground state of  $H_0 + V$ . How should we choose the initial state  $|\phi_j\rangle$  for this to happen? In the non degenerate case, it is often assumed that the ground state of  $H_0$  leads to the ground state of  $H_0 + V$ . When degeneracy is due to the presence of symmetry, band crossing can occur and one should try the  $|\phi_j\rangle$  corresponding to the lowest energy  $E_j^0$  for each irreducible representation. A typical example of band crossing in the presence of symmetry is given by Tanabe-Sugano diagrams of the multiplet theory [21]. For a small crystal field, the ground state has the highest spin value (Hund's rule), but as the crystal field parameter increases, a low spin state can become the ground state.

*Green function.* The expression for the Green function is usually derived under the assumption that the ground state of  $H_0$  is non degenerate [11, 12]. Our adiabatic approximation enables us to determine how this expression is extended to the case of degenerate systems. Now we formally extend our previous results to Fock space.

To follow the usual argument [12], we repeat the calculation by starting from a positively infinite time. In terms of the variable  $s = -\varepsilon|t|$ , the switching function  $e^{-\varepsilon|t|}$  is the same for positive and negative times. As a result, the intertwiner is the same and the only change comes from the phase function:  $U_\varepsilon(0, +\infty)|\phi_j\rangle \simeq e^{-i\theta_j/\varepsilon}A(0, -\infty)|\phi_j\rangle$ . Therefore,

$$\lim_{\varepsilon \rightarrow 0} \frac{U_\varepsilon(0, +\infty)|\phi_j\rangle}{\langle \phi_j | U_\varepsilon(0, +\infty) | \phi_j \rangle} = \frac{A(0, -\infty)|\phi_j\rangle}{\langle \phi_j | A(0, -\infty) | \phi_j \rangle}.$$

In other words, the Gell-Mann and Low wavefunctions obtained from positive and negative infinite times are

equal. This non-trivial result is due to the fact that the switching function  $f(t) = e^{-\varepsilon|t|}$  is even.

The two-point Green function is defined by [12]

$$G(x, y) = \frac{\langle \Psi_{\text{GML}} | O_H | \Psi_{\text{GML}} \rangle}{\langle \Psi_{\text{GML}} | \Psi_{\text{GML}} \rangle},$$

where  $x = (\mathbf{r}, t)$ ,  $y = (\mathbf{r}', t')$  and  $O_H = T(\psi_H(x)\psi_H^\dagger(y))$  is the time-ordered product of fields in the Heisenberg picture. We just showed that this Green function is well defined for any parent state  $|\phi_j\rangle$ . Standard manipulations [12] transform it into

$$G(x, y) = \lim_{\varepsilon \rightarrow 0} \frac{\langle \phi_j | X_\varepsilon | \phi_j \rangle}{\langle \phi_j | U_\varepsilon(+\infty, -\infty) | \phi_j \rangle}, \quad (3)$$

where  $X_\varepsilon = U_\varepsilon(+\infty, t)\psi(x)U_\varepsilon(t, t')\psi^\dagger(y)U_\varepsilon(t', -\infty)$  and  $X_\varepsilon = -U_\varepsilon(+\infty, t')\psi^\dagger(y)U_\varepsilon(t', t)\psi(x)U_\varepsilon(t, -\infty)$  if  $t > t'$  and  $t < t'$ , respectively.

The expression for the Green function generally converges only when the initial state is a parent state. Indeed, consider a state  $|\phi\rangle$  in the model space and write it as  $|\phi\rangle = \sum_j |\phi_j\rangle$ , where  $|\phi_j\rangle = P_j^0|\phi\rangle$ . Thus,

$$U_\varepsilon(0, \pm\infty)|\phi\rangle \simeq \sum_j e^{\mp i\theta_j/\varepsilon}A(0, -\infty)|\phi_j\rangle.$$

If there is more than one  $j$  in the sum, the phases  $\theta_j$  are generally different (in the absence of eigenvalue crossing, they can be shown to be different). Therefore, the phase factors in the numerator and denominator of eq. (3) do not cancel and the expression has no limit for  $\varepsilon \rightarrow 0$ .

*Statistical Green function.* The Green function of the previous section has a non-ambiguous meaning when  $|\phi_j\rangle$  is the parent state of a non-degenerate interacting state. However, when the interacting state itself is degenerate, there is no reason to choose any particular parent state. To solve that problem, Layzer [22] defined the *statistical Green function* as an equal-weight average over the degenerate states. Such a statistical Green function was advocated, for instance, by Alon and Cederbaum [23]. The statistical Green function can preserve the symmetry of the system: in the example of a spherically symmetric Hamiltonian, the Green function obtained from any state  $|\ell m\rangle$  with  $\ell \neq 0$  gives non spherically symmetric charge density, whereas the statistical Green function obtained from the mixed state  $\sum_m |\ell m\rangle(2\ell + 1)^{-1}\langle \ell m|$  gives a spherical charge density [24]. We are now able to prove that the statistical Green function has a well-defined limit when  $\varepsilon \rightarrow 0$ .

To define the statistical Green function of a degenerate interacting system with energy  $E_j(0)$ , we use the density matrix  $\rho = (1/n_j) \sum_{k=1}^{n_j} |\varphi_{jk}^0\rangle\langle \varphi_{jk}^0|$ , where the states  $|\varphi_{jk}^0\rangle$  are those used to calculate  $P_j^0$ . We assume that the degeneracy of  $E_j(0)$  is  $n_j$ . Then,

$$G(x, y) = \lim_{\varepsilon \rightarrow 0} \frac{\text{Tr}(\rho X_\varepsilon)}{\text{Tr}(\rho U_\varepsilon(+\infty, -\infty))}. \quad (4)$$

If we put  $|\phi_j\rangle = |\varphi_{jk}^0\rangle$  in eq. (3), the divergences of the numerator and denominator are  $e^{2i\theta_j/\varepsilon}$ , which *does not depend* on  $k$ . Therefore, they are equal to the divergences of the numerator and denominator of eq. (4), and the statistical Green function is well defined. Note that it is generally not correct to build the statistical Green function from an average over basis states of the full model space.

*Non-equilibrium Green function.* In the study of non-equilibrium systems, it is often convenient to run the evolution operator over a closed time path instead of taking the limit  $t \rightarrow +\infty$ . In this so-called Keldysh approach, the Green function  $\mathcal{G}(x, y)$  is calculated by a formula involving no denominator [25]: it is the limit for  $\varepsilon \rightarrow 0$  of  $\mathcal{G}_\varepsilon = \langle \phi | U_\varepsilon(-\infty, 0) O_H U_\varepsilon(0, -\infty) | \phi \rangle$ . As for the standard Green function, this expression generally converges for degenerate systems only when  $|\phi\rangle$  is a parent state. To see this, we expand again a state of the model space over parent states:  $|\phi\rangle = \sum_j |\phi_j\rangle$ . Then,

$$\mathcal{G}_\varepsilon \simeq \sum_{ij} e^{i(\theta_j - \theta_i)/\varepsilon} \langle \phi_i | A(-\infty, 0) O_H A(0, -\infty) | \phi_j \rangle.$$

This expression converges for  $\varepsilon \rightarrow 0$  when there is a single phase, i.e. when  $|\phi\rangle$  is a parent state. When more than one phase is present, they are usually different and the limit does not exist.

*Conclusion.* The determination of the parent states and the proof of convergence break the last deadlocks in the determination of the Green function of degenerate systems. The main difference with the non-degenerate case is the fact that, for many degenerate systems, the parent state is not a single Slater determinant. To see this, consider a Hamiltonian where  $H_0$  is the restricted Hartree-Fock Hamiltonian of a  $3d^n$  transition metal ion and  $V$  is the sum of the remaining atomic Coulomb interaction and of an effective potential representing the influence of the surrounding atoms. Then, the parent states are exactly the eigenstates of the crystal-field Hamiltonian and they are generally not single Slater determinants. In that case, the structure of the Green function is more complex but powerful combinatorial methods have been recently developed to tackle this problem [26, 27].

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