Many-Body Green Function of Degenerate Systems

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A rigorous nonperturbative 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 nonequilibrium Green function of degenerate systems. The convergence of these Green functions is established.

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Nonperturbative 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 metals 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 six degenerate t_{2g} orbitals (with up and down spins).

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 determine the parent states, i.e., the initial states of H_0 that evolve into eigenstates of H by adiabatically switching the interaction.

Degenerate systems being ubiquitous in quantum physics, this long-standing problem has been discussed 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 also crucial in many-body physics because the Green function of a degenerate system has to be defined from a parent state.

In the present Letter, we give a simple method to explicitly determine the parent states and to define the Green function of degenerate systems. Through a nonperturbative analysis of the evolution operator of a degenerate system, 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 nonperturbative 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 validity of the so-called statistical Green function; (v) the singularity structure of the nonequilibrium 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 nondegenerate ground state $|0\rangle$ of H_0 into an eigenstate $|\Psi_{\mathrm{GML}}\rangle$ of H first proposed by Gell-Mann and Low [13] in 1951

$$|\Psi_{\mathrm{GML}}\rangle = \lim_{\varepsilon\to 0} \frac{U_\varepsilon(0,-\infty)|0\rangle}{\langle 0|U_\varepsilon(0,-\infty)|0\rangle}, \tag{1}$$

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

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

with the initial condition $U_\varepsilon(t',t') = 1$. The wave function $|\Psi_{\mathrm{GML}}\rangle$ 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 $|\Psi_{\mathrm{GML}}\rangle$ for nondegenerate systems was first established 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 $\varepsilon \to 0$, 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.—In this section, we set up the notation and give the theorem that enables us to calculate

the parent states and to define the Green functions. We consider $t \leq 0$ and we rewrite the time-dependent Hamiltonian as $H(s) = H_0 + e^s V$, where $s = \varepsilon t$ is the so-called slow variable. 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 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 $E_j(s)$. For notational convenience, we denote $P_j(-\infty)$ by P_j^0 in the rest of the Letter. The model space M is the vector space generated by the eigenstates corresponding to N_0 eigenvalues of $H_0 = H(-\infty)$. Each eigenvalue of H_0 can be degenerate and is possibly split by the perturbation V, so that the N_0 eigenvalues of H_0 become N eigenvalues $E_1(s), \ldots, E_N(s)$ of $H(s)$, with $N \geq N_0$. Each $E_j(s)$ can be degenerate and the eigenvalues are allowed to cross (Fig. 1). For an octahedral V^{3+} ion, we have $N_0 = 1$ with degeneracy 15, and there are $N = 4$ interacting states: $^1A_{1g}$, ^1E_g, $^1T_{2g}$, and $^3T_{1g}$, with degeneracy $n_j = 1$, 2, 3, and 9, respectively.

A key tool of our approach is $A(s, s_0)$, the rotating frame operator [17,18], that relates the eigenstates at s_0 and s: $A(s, s_0)|\phi_{jk}(s_0)\rangle = |\phi_{jk}(s)\rangle$, so that

$$A(s, s_0)P_j(s_0) = P_j(s)A(s, s_0). \tag{2}$$

Using standard technical assumptions [19], we recently obtained [20] a rigorous approximation of the evolution operator projected on each eigenspace:

$$U_\varepsilon(0, -\infty)P_j^0 \simeq e^{i\theta_j/\varepsilon}A(0, -\infty)P_j^0, \tag{3}$$

where $\theta_j = -\int_{-\infty}^0 [E_j(s) - E_j(-\infty)]ds$. In particular, the divergences of the evolution operator are entirely described by the factor $e^{i\theta_j/\varepsilon}$.

Construction of the parent states.—The parent states are the eigenstates $|\phi\rangle$ of H_0 such that $U_\varepsilon(0, -\infty)|\phi\rangle$ tends to an eigenstate $|\Psi\rangle$ of H, up to a (divergent) phase. Therefore, the parent states are naturally defined in terms of $U_\varepsilon(-\infty, 0)|\Psi\rangle$ and it seems that the interacting states $|\Psi\rangle$ are needed to define the parent states [4,9,21]. We now show that the parent states have a more simple and explicit definition as eigenstates of P_j^0 and we explain how P_j^0 can be calculated by standard time-independent perturbation theory.

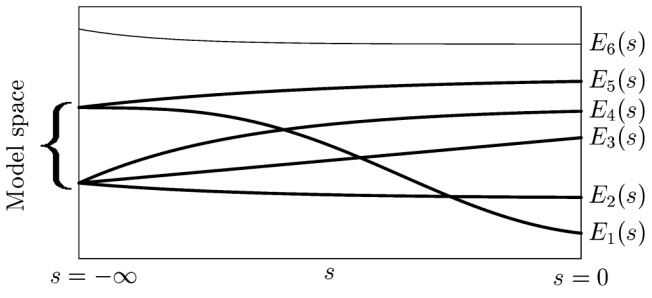

FIG. 1. Example of allowed eigenvalue pattern.

For notational convenience, we denote e^s by λ and the eigenvalues and eigenprojections are written in terms of λ. We denote by $\bar{E}_j(\lambda)$ and $|\bar{\varphi}_{jk}(\lambda)\rangle$ the eigenvalues and eigenstates of $H_0 + \lambda V$ [so that $\bar{E}_j(\lambda) = E_j(s)$]. They can be expanded as [20]

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

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 time-independent 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 $E_j(\lambda)$ and we need more information to determine the n_j states $|\varphi_{jk}^0\rangle$. The Schrödinger equation to order λ 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 λ must be taken into account to determine $|\varphi_{jk}^0\rangle$. In that case, the second order is usually enough [22], but methods have been developed to treat any order [23].

We generally 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 $P_{E_j^0} V P_{E_j^0}$. 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. The computational effort required to construct $|\varphi_{jk}^0\rangle$ is small because it is an eigenvalue problem in a vector space whose dimension is the degeneracy of E_j^0, which is small in applications. From the states $|\varphi_{jk}^0\rangle$ we build the projector P_j^0 and we define a parent state as a state $|\phi\rangle$ such that, for some j,

$$P_j^0|\phi\rangle = |\phi\rangle. \tag{4}$$

In practice, the parent state is one of the $|\varphi_{jk}^0\rangle$.

Generalized Gell-Mann and Low wave function.—We show that the parent states previously defined lead to convergent Gell-Mann and Low wave functions. For a parent state $|\phi_j\rangle$ such that $P_j^0|\phi_j\rangle = |\phi_j\rangle$, Eq. (3) enables us to write

$$\begin{aligned} U_\varepsilon(0,-\infty)|\phi_j\rangle &= U_\varepsilon(0,-\infty)P_j^0|\phi_j\rangle \\ &\simeq e^{i\theta_j/\varepsilon}A(0,-\infty)P_j^0|\phi_j\rangle \\ &\simeq e^{i\theta_j/\varepsilon}A(0,-\infty)|\phi_j\rangle. \end{aligned}$$

Therefore, the following limit exists:

$$|\Psi_{\mathrm{GML}}\rangle = \lim_{\varepsilon\to 0}\frac{U_\varepsilon(0,-\infty)|\phi_j\rangle}{\langle\phi_j|U_\varepsilon(0,-\infty)|\phi_j\rangle} = \frac{A(0,-\infty)|\phi_j\rangle}{\langle\phi_j|A(0,-\infty)|\phi_j\rangle}. \tag{5}$$

The Gell-Mann and Low wave function $|\Psi_{\mathrm{GML}}\rangle$ is indeed an eigenstate of $H_0 + V$ with energy $E_j(0)$ because $P_j(0)|\Psi_{\mathrm{GML}}\rangle = |\Psi_{\mathrm{GML}}\rangle$. To show this, we use Eq. (2):

$$P_j(0)A(0,-\infty)|\phi_j\rangle = A(0,-\infty)P_j^0|\phi_j\rangle = A(0,-\infty)|\phi_j\rangle.$$

In practice, we are interested in the Gell-Mann and Low wave function 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 nondegenerate 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 [24]. 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 functions.—The expression for the Green function is usually derived under the assumption that the ground state of H_0 is nondegenerate [11,12]. Our results enable 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 slow variable $s = -\varepsilon|t|$, the switching function $e^{-\varepsilon|t|}$ is the same for positive and negative times. As a result, the rotating frame operator is the same but the divergent phase changes sign: $U_\varepsilon(0,+\infty)|\phi_j\rangle \simeq e^{-i\theta_j/\varepsilon}A(0,-\infty)|\phi_j\rangle$. Therefore,

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

In other words, the Gell-Mann and Low wave functions obtained from positive and negative infinite times are equal. This nontrivial 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]

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

where $x = (\mathbf{r}, t)$, $y = (\mathbf{r}', t')$, $O_H = T(\psi_H(x)\psi_H^\dagger(y))$ is the time-ordered product of fields in the Heisenberg picture and $|\Psi_{\mathrm{GML}}\rangle$ is defined by Eq. (5). Standard manipulations [12] transform it into

$$G(x,y) = \lim_{\varepsilon\to 0}\frac{\langle\phi_j|X_\varepsilon|\phi_j\rangle}{\langle\phi_j|U_\varepsilon(+\infty,-\infty)|\phi_j\rangle}, \tag{6}$$

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 θ_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. (6) do not cancel and the expression has no limit for $\varepsilon \to 0$.

Statistical Green function.—The Green function of the previous section has a nonambiguous meaning when $|\phi_j\rangle$ is the parent state of a nondegenerate 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 [25] 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 [26]. 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 nonspherically 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 [27]. We are now able to prove that the statistical Green function has a well-defined limit when $\varepsilon \to 0$.

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,

$$G(x,y) = \lim_{\varepsilon\to 0}\frac{\mathrm{Tr}(\rho X_\varepsilon)}{\mathrm{Tr}[\rho U_\varepsilon(+\infty,-\infty)]}. \tag{7}$$

If we put $|\phi_j\rangle = |\varphi^0_{jk}\rangle$ in Eq. (6), the divergences of the numerator and denominator are $e^{2i\theta_j/\varepsilon}$, which does not depend on k. Therefore, the divergent phases of the numerator and denominator of Eq. (7) are equal, and the statistical Green function is well defined. For our octahedral V^{3+} ion, the Green function is defined with the density matrix built from the nine degenerate states with ${}^3T_{1g}$ symmetry if the ion is high spin.

Nonequilibrium Green function.—In the study of nonequilibrium systems, it is often convenient to run the evolution operator over a closed time path instead of taking the limit $t \to +\infty$. In this so-called Keldysh approach, the Green function $\mathcal{G}(x, y)$ is calculated by a formula involving no denominator [28]: it is the limit for $\varepsilon \to 0$ 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 $\varepsilon \to 0$ when there is a single phase, i.e., when $|\phi\rangle$ is a parent state. Otherwise, the limit generally does not exist. The statistical nonequilibrium Green function is defined by using ρ and a trace.

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 nondegenerate 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 because of the so-called initial correlations [29] coming from the matrix elements between the different Slater determinants. Perturbative [29] and nonperturbative [30] methods have been developed to tackle initial correlations. Finally, our approach also gives a nonperturbative proof of the convergence of the effective Hamiltonian [31].

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