

Transforming Nonlocality into a Frequency Dependence: A Shortcut to Spectroscopy

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Measurable spectra are often derived from contractions of many-body Green's functions. One calculates hence more information than needed. Here we present and illustrate an in principle exact approach to construct effective potentials and kernels for the *direct* calculation of electronic spectra. In particular, a dynamical but *local* and *real* potential yields the spectral function needed to describe photoemission. We discuss for model solids the frequency dependence of this “photoemission potential” stemming from the nonlocality of the corresponding self-energy.

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The calculation of electronic excitations and spectra is one of the major challenges of today's condensed matter physics. In fact, while density-functional theory (DFT), especially with simple and efficient approximations like the local-density approximation (LDA) [1], has led to a breakthrough concerning the simulation of ground-state properties, the determination of electronic excited states is still cumbersome. The description of spectroscopy calls for the definition of suitable fundamental quantities (beyond the static ground-state density DFT is built on), and the derivation of new approximations. For neutral excitations (as measured, e.g., in absorption or electron energy-loss spectroscopies) one can in principle work with the *time-dependent* density, and try to approximate time-dependent DFT (TDDFT) [2], for example, in the adiabatic LDA (TDLDA). Also many-body perturbation theory (MBPT) approaches [3], like the GW approximation [4] for the one-particle Green's function or the Bethe-Salpeter equation (BSE) for the determination of neutral excitations, are today standard methods for first-principles calculations of electronic excitations [5]. One of the main reasons for the success of MBPT is the intuitive physical picture that allows one to find working strategies and approximations. Therefore, Green's functions approaches are often used even when one could *in principle* resort to simpler methods, in particular, density-functional based ones—for example, one uses BSE when TDLDA breaks down. It is hence quite logical to try to link both frameworks [6], and derive better approximations for the simpler (e.g., density-functional) approaches from the working approximations of the more complex (e.g., MBPT) ones.

In the present Letter we propose a general framework for the definition of reduced potentials or kernels, designed for obtaining certain quantities that can otherwise be calculated from some N -particle Green's function. In particular, we explore the question of a local and frequency dependent real potential that allows one to find the correct density and trace of the one-particle spectral function and therefore to access direct and inverse photoemission (including the

band gap). We present model results of this new approach for metals and insulators, and discuss the relation to dynamical mean-field theory (DMFT) [7]. Of particular interest is the conversion of nonlocality into frequency dependence that one encounters when an effective potential or kernel with a reduced number of spatial degrees of freedom is used to describe excitations.

In this general scheme we suppose that one wants to calculate the quantity T that is a part of the information carried by the N -particle Green's function G . We symbolically express this relation as $T = p\{G\}$. In the following we will specify the formula for the one-particle G , whereas the completely analogous case of two-particle Green's functions will be briefly discussed at the end. As a well-known example we take the electronic density $T = \rho$ for which the “part” to be taken is the diagonal of the one-particle G : $\rho(rt) = -iG(r, r, t, t^+)$. We then introduce another Green's function G_T which has the part $p\{\cdot\}$ in common with G : $T = p\{G_T\}$. We also suppose that G_T is associated to an effective potential V_T according to $G_T = (\omega - H_0 - V_T)^{-1}$, where H_0 is the Hartree part of the Hamiltonian [8]. The full Green's function G and the new G_T are linked by a Dyson equation:

$$G = G_T + G_T(\Sigma - V_T)G. \quad (1)$$

We now take the part of interest $p\{\cdot\}$ of this Dyson equation. This yields the condition

$$p\{G_T(\Sigma - V_T)G\} = 0. \quad (2)$$

The aim is now to make an ansatz for V_T with a simpler structure than Σ , and for which (2) can be solved. For the example where T is the static density ρ , a static and local potential can do the job. In fact in this example V_T is the exchange-correlation potential $V_{xc}(r)$, G_T is the Kohn-Sham Green's function G_{KS} , and (2) is a well-known result, derived by Sham and Schlüter in [9]. It has subsequently been extended to time-dependent external potentials [10], and employed in many different contexts (see, e.g.,

Refs. [11,12]). The Sham-Schlüter equation (SSE) is still implicit since it is self-consistent in V_{xc} and G_{KS} . Most often it is linearized setting $G = G_{KS}$ everywhere, including in the construction of Σ . This so-called linearized Sham-Schlüter equation, that can also be derived using a variational principle [13,14], is the central equation of the optimized effective potential (OEP) method [15]. In particular, if one uses for Σ the exchange-only approximation $\Sigma = \Sigma_x$, where $\Sigma_x = iG_{KS}v$ (v is the bare Coulomb interaction), one obtains the so-called exact-exchange approximation to V_{xc} [16]. By construction one obtains in this way a good description of the density, whereas there is no reason for other features of the Green's function, in particular, the band gap, to be correct. In our more general scheme one can easily go beyond the case of solely the density. According to the choice of $p\{\cdot\}$, the ansatz for V_T has then to be modified. Below we will first explore the problem of electron addition and removal.

Electronic structure, defined as electron addition and removal energies, is measured by experiments like direct or inverse photoemission. To first approximation [5] these experiments measure the trace of the spectral function $A(r_1, r_2, \omega) = \frac{1}{\pi} |\text{Im}G(r_1, r_2, \omega)|$. In other words, for the interpretation of photoemission spectra one does not need the knowledge of the whole Green's function G , but just the imaginary part of its trace over spatial coordinates together with its full *frequency dependence*. We will hence look for a potential that is simpler than the full self-energy but yields the correct trace of the spectral function. It is reasonable to add the condition that also the density should be correct, which means that the diagonal in real space, and not only its integral, is fixed. Following the general scheme, we introduce a new Green's function $G_{SF} = (\omega - H_0 - V_{SF})^{-1}$ stemming from a potential V_{SF} such that $\text{Im}G_{SF}(r_1, r_1, \omega) = \text{Im}G(r_1, r_1, \omega)$. What degrees of freedom are needed in V_{SF} ? A natural assumption is that V_{SF} should be local in space, but frequency dependent [17,18]. It is also possible to choose V_{SF} to be *real*. With this ansatz Eq. (2) yields

$$V_{SF}(r_1, \omega) = \int dr_2 dr_3 dr_4 \xi^{-1}(r_1, r_4, \omega) \times \text{Im}[G_{SF}(r_4, r_2, \omega)\Sigma(r_2, r_3, \omega)G(r_3, r_4, \omega)], \quad (3)$$

where $\xi(r_1, r_2, \omega) = \text{Im}[G_{SF}(r_1, r_2, \omega)G(r_2, r_1, \omega)]$ [19]. Equation (3) shows that V_{SF} should indeed be frequency dependent unless Σ is *static* and *local* (in that case the ω -dependent terms cancel trivially). Thus, in general a local static (KS) potential will not be able to reproduce the spectral function, whereas $V_{SF}(r, \omega)$ is the local potential that will yield the correct band gap *and* the correct density $\rho(r)$ of the system.

At this point it is interesting to compare our construction with the approach of the spectral density-functional theory (SDFT) [20], where the key variable is the short-range part of the Green's function: $G_{loc}(r, r', \omega) = G(r, r', \omega) \times$

$\Theta(\Omega_{loc})$, where $\Theta(\Omega_{loc})$ is 1 when r is in the unit cell and r' inside a volume Ω_{loc} , and 0 otherwise (see Fig. 1 of Ref. [20]). A new Green's function $G_{SDFT} = (\omega - H_0 - V_{SDFT})^{-1}$ can be introduced such that $G_{SDFT} = G_{loc}$ where G_{loc} is different from 0. Using this property of G_{SDFT} , we find that the (in general complex) potential V_{SDFT} , defined in the volume Ω_{loc} , is

$$V_{SDFT}(r_5, r_6, \omega) = \int_{\Omega_{loc}} dr_1 dr_2 \int dr_3 dr_4 \tilde{G}_{SDFT}^{-1}(r_5, r_1, \omega) \times G_{SDFT}(r_1, r_3, \omega)\Sigma(r_3, r_4, \omega) \times G(r_4, r_2, \omega)\tilde{G}^{-1}(r_2, r_6, \omega) \quad (4)$$

where \tilde{G}^{-1} , if it exists, is the local inverse of G in Ω_{loc} (while G^{-1} would be the full inverse, defined in the whole space). In principle SDFT is a formally exact theory. The most common approximation to SDFT is the dynamical mean-field theory [7], which corresponds to a linearization in G_{loc} .

In the limit case that Σ is completely localized in Ω_{loc} , then V_{SDFT} and G_{SDFT} coincide, respectively, with Σ and G . The interesting situation is of course when this is not true. In fact, our V_{SF} of Eq. (3) corresponds to the case where $\Omega_{loc} \rightarrow 0$ so that this condition is certainly not fulfilled. Then, as we will illustrate below, the nonlocality of Σ will strongly influence V_{SF} and, in particular, lead to a frequency dependence which is *not* the frequency dependence of Σ itself. This will to a certain extent also be true for any Ω_{loc} of finite range, so that the following discussions may also give useful insight for research in the field of DMFT.

To illustrate the frequency dependence of V_{SF} we consider the case of homogeneous systems, where all local quantities (like V_{xc} and V_{SF}) are constant in space. In particular, the xc potential is $V_{xc} = \Sigma(p = p_F, \omega = 0)$, while, since $V_{SF} = V_{SF}(\omega)$, one can directly write (here and throughout the Letter we adopt atomic units):

$$|\text{Im}G_{SF}(r, r, \omega)| = 2 \int \frac{d_3p}{8\pi^3} \pi \delta(\omega + \mu - p^2/2 - V_{SF}(\omega)) = \frac{\sqrt{2}}{\pi} \theta(\omega + \mu - V_{SF}(\omega)) \times \sqrt{\omega + \mu - V_{SF}(\omega)}. \quad (5)$$

Requiring that this is equal to $|\text{Im}G(r, r, \omega)|$, one finds a unique local potential V_{SF} [for $V_{SF}(\omega) < \omega + \mu$]:

$$V_{SF}(\omega) = \omega + \mu - \left(\frac{\pi}{\sqrt{2}} |\text{Im}G(r, r, \omega)| \right)^2. \quad (6)$$

It is first of all interesting to consider the case of simple metals, that can be modeled by a homogeneous electron gas (HEG). Here, we will assume a static but nonlocal self-energy: $\Sigma_\lambda(r - r') = iG(r - r', 0^+)v_\lambda(r - r')$, that is a screened-exchange-like form where the screened Coulomb potential is $v_\lambda(r - r') = v(r - r')e^{-|r-r'|/\lambda}$. For a larger screening length λ , Σ is more effectively

nonlocal, since less screened. λ tunes the effective range of the interaction: from $\lambda = 0$ ($\Sigma = 0$, Hartree approximation), to $\lambda = \infty$ (unscreened Hartree-Fock approximation). Using the relation (6) we calculate $V_{\text{SF}}(\omega)$ for different values of λ , i.e., for different nonlocality ranges of Σ (see Fig. 1). We find that the spatial nonlocality of the static self-energies is completely transformed into the frequency dependence of V_{SF} . This is an essential property of V_{SF} , which radically distinguishes V_{SF} from the static V_{xc} . In particular, looking at Fig. 1, one observes that the more nonlocal Σ_λ is, the more dynamical V_{SF} becomes. This is confirmed by comparing two materials: aluminum and sodium.

The HEG is a prototype of metallic systems. Let us consider the simplest model insulator introduced by

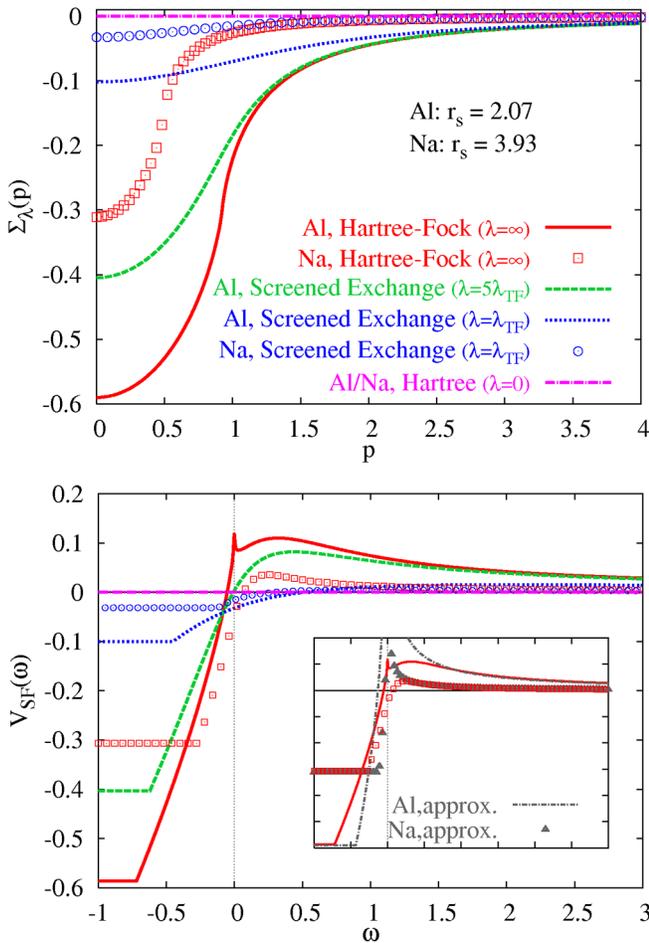


FIG. 1 (color online). Transformation of nonlocal statically screened-exchange self-energy $\Sigma_\lambda(p)$ (upper panel) to the frequency dependent local $V_{\text{SF}}(\omega)$ (bottom panel), for different screening lengths λ in HEG [$\lambda_{\text{TF}} = (4p_F/\pi)^{-1/2}$ is the Thomas-Fermi length], and densities corresponding to aluminum (lines) and sodium (open symbols). The key is common to both panels. The ω dependence of V_{SF} is stronger for more nonlocal self-energies. Below band edges, where $\text{Im}G = 0$, $V_{\text{SF}}(\omega)$ has been defined continuous and equal to a constant $> \omega + \mu$. In the inset: comparison between the exact and approximated solutions (6) and (8) in the Hartree-Fock case.

Callaway [21]. The Callaway’s model is obtained from HEG by inserting a gap Δ between the occupied “valence” states $\phi_v(r)$ ($p < p_F$) and the “conduction” states $\phi_c(r)$ ($p > p_F$). Within the Green’s functions formalism this corresponds to a nonlocal static “scissor” self-energy

$$\Sigma(r, r') = \Delta \sum_c \phi_c(r) \phi_c^*(r'), \quad (7)$$

which rigidly shifts all conduction states, and produces a gap between the valence, $E_v = \varepsilon_F = \mu$, and the conduction, $E_c = \varepsilon_F + \Delta$, band edges. Because of the homogeneity of the model, Eq. (6) is still applicable. From Eq. (6), one gets that $V_{\text{SF}}(\omega) = 0$ for $\omega < E_v - \mu = 0$ and $V_{\text{SF}}(\omega) = \Delta$ for $\omega > E_c - \mu = \Delta$. Between $\omega = 0$ and $\omega = \Delta$, where $\text{Im}G(\omega) = 0$, there are many different choices for $V_{\text{SF}}(\omega)$: from (5) it is enough that $V_{\text{SF}}(\omega) \geq \omega + \mu$ to get $\text{Im}G_{\text{SF}}(\omega) = 0$. In any case a static constant potential, like V_{xc} , cannot produce the correct band gap, because at $E_v - \mu$ and $E_c - \mu$ it should assume different values. The only effect of V_{xc} with respect to H_0 would be just a rigid shift of the whole band structure and no gap could be opened. In fact, Δ in (7) corresponds to the derivative discontinuity of V_{xc} when an electron is added to the system: $\Delta = V_{\text{xc}}^{(N+1)}(r) - V_{\text{xc}}^{(N)}(r)$ [11]. Our simple example demonstrates that this discontinuity, which constitutes the difference between the true quasiparticle gap and the Kohn-Sham one, is accounted for by the potential V_{SF} rightly through its frequency dependence.

Knowing the exact solutions, one can also verify how common approximations to SSE perform with these strongly frequency dependent functions, in particular, when we linearize the SSE by setting $G = G_{\text{SF}}$ everywhere (in DFT this would correspond to the OEP approach). The linearized SSE is still self-consistent in V_{SF} and G_{SF} . Yet we can approximate it at the first order setting G and G_{SF} equal to the Hartree G_H . In the Hartree-Fock case in HEG, we get, for $\omega > -\varepsilon_F$:

$$V_{\text{SF}}\left(\tilde{\omega} = \frac{\omega + \varepsilon_F}{\varepsilon_F}\right) = -\frac{2p_F}{\pi} \left(1 + \frac{\sqrt{\tilde{\omega}}}{2} \ln \left| \frac{\sqrt{\tilde{\omega}} - 1}{\sqrt{\tilde{\omega}} + 1} \right| \right), \quad (8)$$

which shows a logarithmic divergence at the Fermi energy $\omega = 0$ and hence is very different from the exact solution (see the inset of Fig. 1). The approximated V_{SF} in HEG is distant from the exact one also when the linearized SSE is solved self-consistently. The agreement should improve when screening is taken into account, since then V_{SF} is less frequency dependent and G_{SF} is much closer to G and G_H . Already for sodium the agreement is better than for aluminum. In any case, these results demonstrate that the linearization of the generalized SSE is a delicate procedure. In the following we will, however, show that it works very well in certain cases, for example, for the kernel f_{xc} of TDDFT.

Up to now we have considered Dyson equations only for the one-particle Green’s function. The generalization of

SSE can, however, be applied to any Dyson-like equation, for example, involving two-particle Green's functions, like the four-point reducible polarizability ${}^4\chi_{\text{MB}}$. In this way we can derive an exact equation for the kernel $f_{\text{xc}} = f_{\text{xc}}^{(1)} + f_{\text{xc}}^{(2)}$ of TDDFT. In particular, following Ref. [6], we concentrate on the term $f_{\text{xc}}^{(2)}$ that describes electron-hole interactions. This means that in the TDDFT polarizability ${}^4\chi_{\text{TD}}$ the ‘‘gap opening’’ contribution due to the term $f_{\text{xc}}^{(1)}$ is already included by using $\chi_0^{\text{QP}} = -iGG$ instead of the KS independent particle polarizability. $f_{\text{xc}}^{(2)}$ is the two-point kernel that gives the correct *two-point* polarizability [22]: ${}^4\chi_{\text{TD}}(1122) = {}^4\chi_{\text{MB}}(1122) \equiv \chi(12)$. Applying this condition to the Dyson equation ${}^4\chi_{\text{MB}} = {}^4\chi_{\text{TD}} + {}^4\chi_{\text{TD}}[F_{\text{MB}} - f_{\text{xc}}^{(2)}]{}^4\chi_{\text{MB}}$ yields the generalized SSE, and hence the exact expression of $f_{\text{xc}}^{(2)}$:

$$f_{\text{xc}}^{(2)}(34) = \chi^{-1}(31){}^4\chi_{\text{TD}}(1156)F_{\text{MB}}(5678) \\ \times {}^4\chi_{\text{MB}}(7822)\chi^{-1}(24), \quad (9)$$

where $F_{\text{MB}} = i\delta\Sigma/\delta G$ is the exchange-correlation part of the kernel of the Bethe-Salpeter equation, which, in the framework of *ab initio* calculations [5], is most frequently approximated by: $F_{\text{MB}}(1234) = -W^{\text{st}}(12)\delta(13)\delta(24)$ where $W^{\text{st}}(12) = W(r_1, r_2, \omega = 0)\delta(t_2 - t_1^+)$ is the statically screened Coulomb interaction. An approximated expression for $f_{\text{xc}}^{(2)}$, obtained from the linearized generalized SSE, where we set $\chi(12) = \chi_0^{\text{QP}}(12)$ and $\chi^3(1; 23) = {}^4\chi_{\text{MB}}(1123) = {}^4\chi_{\text{TD}}(1123) = {}^4\chi_0^{\text{QP}}(1123) = -iG(12)G(31)$, is then

$$f_{\text{xc}}^{(2)}(\omega) = (\chi_0^{\text{QP}})^{-1}(\omega)\chi^3(\omega)W(0)^3\chi(\omega)(\chi_0^{\text{QP}})^{-1}(\omega). \quad (10)$$

In this equation only the frequency dependence of the various terms has been put into evidence, since it is mostly interesting to note that, although W and hence F_{MB} are static, f_{xc} is frequency dependent unless W is short-ranged, in which case the frequency dependence of the other components cancels. This recalls the analogous transformation of static self-energies into frequency dependent potentials discussed above. Equation (10) represents a new derivation of a two-point linear response exchange-correlation kernel that has previously been obtained in several other ways [23]. It has been shown to yield absorption or energy-loss spectra of a wide range of materials in very good agreement with experiment [23]. This means also that the linearization of the generalized SSE in this case turns out to be a very good approximation. The present derivation is particularly quick and straightforward, showing one of the advantages of the generalized Sham-Schlüter equation formulation.

In conclusion, in this Letter we propose a shortcut for the calculation of electronic spectra, based on a generalization

of the Sham-Schlüter equation [9]. In particular, we have introduced a *local* and *real* potential for photoemission, with a frequency dependence stemming both from the frequency dependence and from the *nonlocality* of the underlying self-energy. We have illustrated some features at the example of model systems. We have also applied the approach to the derivation of an exchange-correlation kernel for the calculation of absorption spectra. This work opens the way to explore new approximations for simplified potentials and kernels that can be employed to calculate a wide range of electronic spectra.

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