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 in simple and very 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 quite cumbersome. Static ground-state DFT is not the adequate approach to spectroscopy. On the other hand, the full solution of the many-body Schrödinger equation for systems of more than some tens of atoms is today out of reach. Clearly, 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 then try to approximate this Time-Dependent DFT (TDDFT), for example in the adiabatic LDA (TDLDA). Also Many-Body Perturbation Theory (MBPT) approaches [2], like the GW approximation [3] 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 [4]. One of the main reasons for their success is their 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 more simplified methods, in particular density-functional based ones - for example, when TDLDA breaks down. It is hence quite logical to try to link both frameworks [5], and derive better approximations for the simpler (e.g. density-functional) approaches from the working approximations of the more complex (e.g. MBPT) ones. Two prominent examples for such a procedure are the optimized effective potential (OEP) method [6] where a local and static KS potential is obtained from an in principle nonlocal and frequency dependent self-energy, and recent derivations in TDDFT of a two-point linear response xc kernel from the four-point BSE [7]. These constitute, at least at first sight, distinct methods that solve particular questions and leave other, very important points unsolved. The best example for such an open problem is probably the so-called “band-gap problem” [8] of the Kohn-Sham (KS) [1] approach: one would like to have a simple potential that yields not only the correct density, but also band gaps in agreement with experiment. Although OEP in the exact-exchange approximation (EXX) [9] had yielded some promising results in this direction, it is clear that a systematic solution has not yet been found [10].

In the present work 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. We show that both the abovementioned OEP and the TDDFT kernel from MBPT are particular cases of our approach. As a new level, we explore the question of a local and frequency dependent real potential that allows one to find the correct trace of the one-particle spectral function and therefore access direct and inverse photoemission (including the bandgap). We present results of this new approach for simple metals and a model insulator, and discuss the relation to dynamical mean-field theory (DMFT) [11]. 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 now suppose that we want 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 $T = p$ for which the “part” to be taken is the diagonal of the one-particle $G$: $\rho(r) = -iG(r,t,t^*)$. We then introduce another Green’s function $G_T$ which has the part $p\{\}$ 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 Hamiltonian \[21\]. The full Green’s function $G$ and the new $G_T$ are linked by a Dyson equation:

$$G = G_T + G_T (\Sigma - V_T) G$$

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

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

The aim is now to make an ansatz for $V_T$ with a simpler structure than $\Sigma$, and for which \[2\] can be solved. For the example where $T$ is the density $\rho$, 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 function $G_{KS}$, and \[2\] is a well-known result, derived by Sham and Schlüter in \[12\]. It has subsequently been extended to time-dependent external potentials \[13\], and employed in many different contexts (see e.g. Refs. \[8\], \[14\]). The Sham-Schlüter equation (SSE) is still implicit since self-consistent in $V_{xc}$ and $G_{KS}$. Most often it is linearized setting $G = G_{KS}$ everywhere, including in the construction of $\Sigma$. This so called linearized Sham-Schlüter equation, that can also be derived using a variational principle \[15\], \[16\], is the central equation of the OEP method \[8\]. In particular, if one uses for $\Sigma$ the exchange-only approximation $\Sigma = \Sigma_r$, where $\Sigma_r = iG_{KS} v$ (v is the bare Coulomb interaction), one obtains the so called exact-exchange approximation to $V_{xc}$ \[2\]. Obviously, 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. However, in our much more general scheme one can easily go beyond the case of solely the density $\rho(r)$. According to the choice of $p\{\}$, 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 \[4\] these experiments measure the trace of the spectral function $A(r_1, r_2, \omega) = \frac{1}{2} \text{Im} G(r_1, r_2, \omega)$. In other words, for the interpretation of photoemission spectra one doesn’t 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 smaller 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. \[4\] yields:

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

where $\xi(r_1, r_2, \omega) = \text{Im}\{ G_{SF}(r_1, r_2, \omega) G(r_2, r_1, \omega) \}$. The solution exists if $\xi$ is invertible. Whether this is always the case is a delicate question and beyond the scope of the present work. Equation (3) shows that $V_{SF}$ should indeed be frequency dependent unless $\Sigma$ is static and local (in that case the $\omega$-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 bandgap 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) \[19\], where the key variable is the short-range part of the Green’s function: $G_{loc}(r, r', \omega) = G(r, r', \omega) \Theta(\Omega C)$, where $\Theta(\Omega C)$ is 1 when $r$ is in the unit cell and $r'$ inside the volume $\Omega_C$, and 0 otherwise (see Fig. 1 of Ref. \[19\]). 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 $\Omega_C$, is:

$$V_{SDFT}(r_5, r_6, \omega) = \int_{\Omega_C} dr_1 dr_2 \int dr_3 dr_4 \tilde{G}_{SDFT}^{-1}(r_5, r_1, \omega) G_{SDFT}(r_1, r_3, \omega) \Sigma(r_3, r_4, \omega) G(r_4, r_2, \omega) \tilde{G}^{-1}(r_2, r_6, \omega)$$ (4)
where \( G^{-1} \), if it exists, is the local inverse of \( G \) in \( \Omega_C \), (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 [11]. In this perspective [19] DMFT can be viewed as consisting in the assumption of taking for the interaction energy functional of SDFT \( \Phi_{SDFT}[G_{loc}] \) the form of functional \( \Phi_{MB}[G] \) for the full Green’s function \( G \). This means that the shorter the range of the self-energy, is, the better this approximation becomes. In particular, in the limit case that \( \Sigma \) is completely localized in \( \Omega_C \), then \( V_{SDFT} \) and \( G_{SDFT} \) coincide respectively with \( \Sigma \) and \( G \). The interesting situation is of course when this is not true. In fact, our \( V_{SF} \) of Eq. (6) corresponds to the case where \( \Omega_C \rightarrow 0 \) so that this condition is certainly not fulfilled. Then, as we will illustrate below, the nonlocality of \( \Sigma \) will strongly influence \( V_{SF} \) and in particular lead to a frequency dependence which is not the frequency dependence of \( \Sigma \) itself. This will to a certain extent also be true for any \( \Omega_C \) 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 paper we adopt atomic units):

\[
[\text{Im} G_{SF}(r, \omega)] = 2 \int \frac{d^3p}{8\pi^3} \pi \delta(\omega + \mu - p^2/2 - V_{SF}(\omega)) = \frac{\sqrt{2}}{\pi} \theta(\omega + \mu - V_{SF}(\omega)) \sqrt{\omega + \mu - V_{SF}(\omega)}. \tag{5}
\]

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

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

It is first of all interesting to consider the case of simple metals, that can be modelled by a homogeneous electron gas. Here, we will assume a static but nonlocal self-energy [22]: \( \Sigma_{\lambda}(r - r') = iG(r - r', t - t^+)v_\lambda(r - r') \), 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 \( \lambda, \Sigma \) is more effectively nonlocal, since less screened. \( \lambda \) tunes the effective range of the interaction: from \( \lambda = 0 \) \((\Sigma = 0, \text{Hartree approximation})\), to \( \lambda = \infty \) (unscreened Hartree-Fock). Using the relation [20] we calculate \( V_{SF}(\omega) \) for different values of \( \lambda \), i. e. for different nonlocality ranges of \( \Sigma \) (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 \( \Sigma_{\lambda} \) is, the more dynamical \( V_{SF} \) becomes. This is confirmed by comparing two materials: aluminium and sodium.

The HEG is a prototype of metallic systems. Let us consider the simplest model insulator introduced by Callaway [21]. The Callaway’s model is obtained from HEG by inserting a gap \( \Delta \) 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:

\[
\Sigma(r, r') = \Delta \sum_c \phi_c(r)\phi_c^*(r'), \tag{7}
\]

which rigidly shifts all conduction states, and produces...
a gap between the valence, \( E_v \), and the conduction, \( E_c = \varepsilon_F + \Delta \), band edges. Due to the homogeneity of the model, Eq. (8) is still applicable. From Eq. (8), one gets that \( V_{SF}(\omega) = 0 \) for \( \omega < E_v - \mu = 0 \) and \( V_{SF}(\omega) = \Delta \) for \( \omega > E_c - \mu = \Delta \). Between \( \omega = 0 \) and \( \omega = \Delta \), where Im\( G(\omega) = 0 \), there are many different choices for \( V_{SF}(\omega) \): from Eq. (8) it is enough that \( V_{SF}(\omega) \geq \omega + \mu \) to get Im\( G(\omega) = 0 \). In any case a static constant potential, like \( V_{xc} \), cannot produce the correct bandgap, 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 bandstructure and no gap could be opened. In fact, \( \Delta \) in (7) corresponds to the discontinuity, 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 aluminium. 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 \( 4\chi_{MB} \). In this way we can derive an exact equation for the kernel \( f_{xc} = f_{xc}^{(1)} + f_{xc}^{(2)} \) of TDDFT. In particular, following Ref. [8], we concentrate on the term \( f_{xc}^{(2)} \) that describes electron-hole interactions. This means that in the TDDFT polarizability \( 4\chi_{TD} \) the “gap opening” contribution due to the term \( f_{xc}^{(1)} \) is already included by using \( \chi_0^{QP} = -iGG \) instead of the KS independent particle polarizability. \( f_{xc}^{(2)} \) is the two-point kernel that gives the correct two-point polarizability [23]. \( 4\chi_{TD}(1122) = 4\chi_{MB}(1122) \equiv \chi(12) \). Applying this condition to the Dyson equation \( 4\chi_{MB} = \chi_{TD}(F_{MB} - f_{xc}^{(2)})^4\chi_{MB} \) yields the generalized SSE, and hence the exact expression of \( f_{xc}^{(2)} \):

\[
f_{xc}^{(2)}(34) = \chi^{-1}(31)4\chi_{TD}(1156)F_{MB}(5678)\times4\chi_{MB}(7822)\chi^{-1}(24),
\]

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

\[
f_{xc}^{(2)}(\omega) = (\chi_0^{QP})^{-1}(\omega)\chi^4(\omega)W(0)^3\chi(\omega)(\chi_0^{QP})^{-1}(\omega).
\]

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 [3]. It has been shown to yield absorption or energy-loss spectra of a wide range of materials in very good agreement with experiment [2]. 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-Schlütter equation formulation.

In conclusion, in this paper we propose a shortcut for the calculation of electronic spectra, based on a generalization of the Sham-Schlütter equation [12]. 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 non-locality of the underlying self-energy. We have illustrated some features at the example of sodium and aluminium. 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.
We are grateful for discussions with R. Del Sole, G. Onida, F. Sottile, and F. Bruneval, and support from the EU’s 6th Framework Programme through the NANOQUANTA Network of Excellence (NMP4-CT-2004-500198) and from ANR (project NT0S-3_43900).

[1] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
[2] A. L. Fetter and J. D. Walecka, Quantum Theory of Many-Particle Systems (McGraw-Hill, New York, 1971).
[3] L. Hedin, Phys. Rev. 139, A796 (1965).
[4] G. Onida, L. Reining, and A. Rubio, Rev. of Mod. Phys. 74, 601 (2002).
[5] F. Bruneval et al., Phys. Rev. Lett. 94, 186402 (2005).
[6] R. T. Sharp and G. K. Horton, Phys. Rev. 30, 317 (1953).
[7] M.A.L. Marques et al., Eds., Time-Dependent Density Functional Theory (Springer, Berlin Heidelberg, 2006), and references therein.
[8] R. W. Godby, M. Schlüter, and L.J. Sham, Phys. Rev. Lett. 56, 2415 (1986); Phys. Rev. B 36, 6497 (1987).
[9] A. Görling, J. Chem. Phys. 123, 062203 (2005), and references therein.
[10] M. Grüning, A. Marini and A. Rubio, J. Chem. Phys. 124, 154108 (2006).
[11] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. 68, 13 (1996).
[12] L. J. Sham and M. Schlüter, Phys. Rev. Lett. 51, 1888 (1983); L.J. Sham, Phys. Rev. B 32, 3876 (1985).
[13] R. van Leeuwen, Phys. Rev. Lett. 76, 3610 (1996).
[14] I. V. Tokatly and O. Pankratov, Phys. Rev. Lett. 86, 2078 (2001).
[15] M. E. Casida, Phys. Rev. A 51, 2005 (1995).
[16] U. von Barth et al., Phys. Rev. B 72, 235109 (2005).
[17] L. J. Sham and W. Kohn, Phys. Rev. 145, 561 (1966).
[18] W. E. Pickett and C.S. Wang, Phys. Rev. B 30, 4719 (1984).
[19] S. Y. Savrasov and G. Kotliar, Phys. Rev. B 69, 245101 (2004), and references therein.
[20] J. Callaway, Phys. Rev. 116, 1368 (1959).
[21] Here we implicitly assume that $G$ and $G_T$ yield the same density, but this hypothesis can be straightforwardly generalized.
[22] In order to make a comparison with experimental results we should consider self-energies that include dynamical correlations. Such an additional frequency dependence in $\Sigma$ would trivially add to the frequency dependence of $V_{SF}$.
[23] One has to be careful about the link between time-ordered and retarded quantities.