On the initial stage of quasiparticle decay

Y. Pavlyukh* and J. Berakdar
Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany

A. Rubio
Nano-Bio Spectroscopy Group and ETSF Scientific Development Centre,
Dpto. de Física de Materiales, Universidad del País Vasco,
CFM CSIC-UPV/EHU-MPC and DIPC, Av. Tolosa 72, E-20018 San Sebastián, Spain
(Dated: June 6, 2011)

Generally, the addition or removal of a single particle in a many-body system does not correspond to an exact eigenstate of the system. Thus the resulting coherent excitation evolves in time. As discussed here, the evolution at short times upon the excitation with the energy \( \epsilon \) exhibits a quadratic decay (with the rate constant \( \gamma(\epsilon) \)). Later on, after some time \( \tau(\epsilon) \), the exponential decay sets in. It is governed by another rate constant \( \gamma(\epsilon) \). This behavior is generic for many realistic finite and extended systems. For a finite system it is possible to assess this behavior full numerically using an exact solution of the many-body problem. We present a simple model for the electron spectral function that links together all three aforementioned parameters and give a prescription how the energy uncertainty \( \sigma^2(\epsilon) \) can be computed within the many-body perturbation theory. Our numerical results demonstrate that the model approach accurately reproduces the exact spectral function in a large range of energies even in the case of fragmented many-body states. We show that the central quantity of this study \( \sigma^2(\epsilon) \) can easily be computed exactly or from approximate theories and, hence, can be used for their validation.

We also point out how the set in time can be tested by means of attosecond spectroscopy.

PACS numbers: 71.10.-w,31.15.A-,71.10.Ay, 73.22.Dj

I. INTRODUCTION

Undoubtedly, one of the most exciting development over the last decade has been the development of time-resolved spectroscopic techniques with the attosecond resolution (Refs. 1–3 and references therein). This opens the door to address questions regarding the nature of the formation, evolution, and decay of electronic states which in essence govern the optical, transport and magnetic properties of matter. For instance, in Ref. 4 it has been shown experimentally for a tungsten surface that the photoelectrons emitted from a core instance, in Ref. 4 it has been shown experimentally for a tungsten surface that the photoelectrons emitted from a core state that the photoelectrons emitted from a core state emits with a time delay of \( t \). After some time \( \tau \), the exponential decay sets in. It is governed by another rate constant \( \gamma(\epsilon) \). This behavior is generic for many realistic finite and extended systems. For a finite system it is possible to assess this behavior full numerically using an exact solution of the many-body problem. We present a simple model for the electron spectral function that links together all three aforementioned parameters and give a prescription how the energy uncertainty \( \sigma^2(\epsilon) \) can be computed within the many-body perturbation theory. Our numerical results demonstrate that the model approach accurately reproduces the exact spectral function in a large range of energies even in the case of fragmented many-body states. We show that the central quantity of this study \( \sigma^2(\epsilon) \) can easily be computed exactly or from approximate theories and, hence, can be used for their validation.

We also point out how the set in time can be tested by means of attosecond spectroscopy.

This, however, holds true only for times \( t \gg 1/\gamma \), which excludes the set-in regime right after the excitation. The importance of this restriction is illustrated by the following: Let us assume an exponential decay at all \( t \), thus the QP peak appears in frequency with a Lorentzian shape. This means that at the QP energy \( \epsilon \) the spectral function behaves as

\[
A_L(\omega; \epsilon) = \frac{1}{\pi} \frac{\gamma}{(\omega - \epsilon)^2 + \gamma^2}.
\]

The standard deviation \( \sigma^2(\epsilon) \) of the spectral density given by such a functional form diverges,

\[
\sigma^2(\epsilon) = \int_{-\infty}^{\infty} d\omega (\omega - \epsilon)^2 A_L(\omega; \epsilon) \rightarrow \infty.
\]  

(1)

Explicit calculations for a three-dimensional (3D) homogeneous electron gas (HEG) show that this divergence is spurious and that the zero, first and second spectral moments are indeed finite. The convergence of the integral Eq. (1) is governed by the high-frequency behavior of the spectral function. Thus, the short-time limit of the single particle Green’s function (from which \( A_L \) derives) is of a particular interest. Quantum-kinetics indicates a quadratic decay in time. It is conceivable that the above arguments can be repeated for states appearing with a Lorentzian spectral shape, even for few-body systems. Hence, measuring the initial time evolution, i.e. right after one electron has been removed or added, yields information beyond the spectral distribution of the states. It is our goal to quantize that information in terms of physical processes and offer a scheme for their computation. As an example we perform calculations for small metal clusters.
II. THE SPECTRAL FUNCTION

The spectral function of a fermionic many-body quantum system is defined in its most general form as the overlap of a particle and hole states:

\[
S_{ij}(t-t') = \frac{1}{2\pi} \langle (H_i(t)H_j(t')) + (P_i(t)P_j(t')) \rangle.
\]

(2)

The states emerging by adding \((|P_i(t)\rangle = |\hat{\psi}_i^\dagger(t)\rangle_{\text{GS}}\) or removing \((|H_i(t)\rangle = |\hat{\psi}_i(t)\rangle_{\text{GS}}\) a particle in the ground state are not the eigenstates of the system in general and, thus, decay in time. Typically, the single-particle basis can be constructed so that the matrix (2) is nearly diagonal (for homogeneous translationary-invariant systems it is true in general) and we can label its elements by the corresponding state energies. Furthermore, it is convenient to represent the spectral function as a product of a noninteracting oscillatory part and a decaying part \(A(t; \epsilon)\):

\[
S(t; \epsilon) = e^{-i\epsilon t} A(t; \epsilon).
\]

(3)

While the exponential decay in the long-time limit:

\[
A(t; \epsilon) \xrightarrow{t \to \infty} e^{-\gamma t}.
\]

(4)

is a renown feature of Fermi liquids there are no evidences for universal short-time limit. In general, \(A(t; \epsilon)\) is a complicated non-analytic function in the vicinity of \(t = 0\). However, these complications can only arise as a result of integration over infinitely many scattering channels of the quasiparticle decay. In finite systems, or when a quasiparticle decays due to the interaction with a bounded spectrum of bosonic excitations such as longitudinal optical phonons\(^{10}\) or plasmons\(^{11}\) the function is well-behaved. The lowest order cumulant expansion for the Green’s function leads then to the quadratic decay:

\[
\frac{d}{dt} A(t; \epsilon) \xrightarrow{t \to 0} -\sigma^2(\epsilon) t.
\]

(5)

In the present work we propose a model spectral function that exhibits the correct short and long-time behavior, demonstrate how its parameters can be computed based on the many-body perturbation theory and present numerical results for a finite system as an illustration for the accuracy of the theory and as a justification of further approximations. An attempt with a similar goal has been undertaken in Ref. 10, the resulting spectral function, however, violates the sum rules and has a shape with the spectral moments finite at any order, at variance with Ref. 8. The spectral function given in this work fulfill all sum rules and comply with the exact short and long time-limits. In fact, in a recent work\(^{12}\) we discussed and justified this ansatz for a homogenous electron gas. The key ingredients are the imaginary part of the on-shell electron self-energy \(\gamma(\epsilon) = \text{Im} \Sigma(\omega = \epsilon; \epsilon)\) and the decay constant \(\sigma^2(\epsilon)\) as expressed in terms of the zeroth spectral moment of the self-energy \(\Sigma^{(0)} = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega |\text{Im} \Sigma(\omega; \epsilon)|\). The approach provides a recipe to compute the short-time limit of the electron correlation function on the basis of many-particle perturbation theory. In particular, we demonstrate how the decay constant (Eq. 5) can be computed diagrammatically to any desired order in the interaction. Conceptually, the problem should be addressed by the quantum kinetic theory. However in this formalism, analytic calculations of the initial stage of the quasiparticle are not available and numerical approaches rely on further approximations.\(^{13-15}\)

III. MODEL SPECTRAL FUNCTION

By the definition (2) the spectral function fulfills \(S^*(t; \epsilon) = S(-t; \epsilon)\) and thus in the frequency domain \(S(\omega; \epsilon)\) is real and positive. For the decaying part (3) we make an ansatz

\[
A(t; \epsilon) = \exp \left( -\gamma(\epsilon) \frac{t^2}{t + \tau(\epsilon)} \right), \quad \text{for } t > 0,
\]

(6)

which obeys the two limiting cases [Eqs. (5,4)] with \(\sigma^2(\epsilon) = 2\gamma/\tau\). The Fourier transform of the spectral function can be written as follows:

\[
\hat{A}(\omega; \epsilon) = \frac{1}{\pi} \int_0^\infty \cos[(\omega - \epsilon)t] A(t; \epsilon) dt.
\]

(7)

For \(A(t; \epsilon)\) given by Eq. (6) the analytic form of the Fourier transform is not known, but can easily be obtained numerically [Fig. (1)] and it is also possible to prove its positivity.\(^{16,17}\) Its odd spectral moments are zero because of symmetry consideration \(A(t; \epsilon) = A(-t; \epsilon)\):

\[
\hat{M}^{(2k-1)}(\epsilon) = \int_{-\infty}^{\infty} d\omega (\omega - \epsilon)^{2k-1} A(\omega; \epsilon) = 0.
\]
Thus $M^{(1)}(e) = M^{(0)}(e) - \epsilon = 0$. The even spectral moments can analytically be obtained from the derivatives of $A(t; e)$ at $t = 0$:

$$M^{(2k)}(e) = \int_{-\infty}^{\infty} d\omega (\omega - e)^{2k} A(\omega; e) = (-1)^k \lim_{t \to 0} A^{(2k)}(t; e).$$

This leads to $M^{(0)}(e) = M^{(0)}(e) = 1$ (normalization condition), and $M^{(2)}(e) = M^{(2)}(e) - [M^{(1)}(e)]^2 = \frac{2\tau_1}{\pi\gamma}$. Higher spectral moments diverge because of the discontinuity of the derivative of $A(t; e)$ at $t = 0$. This completes the proof that in the frequency domain it has exactly three finite spectral moments in accordance with Ref. 8. The asymptotic large-$\omega$ expansion can be obtained by integrating Eq. (7) by parts:

$$A(\omega; e) \sim \frac{6}{\pi} \frac{\gamma}{(\omega - e)^3} \text{ as } \omega \to \infty.$$  

According to Altshuler et al.\textsuperscript{18} the initial stage of the quasiparticle decay involves a formation of the two-particle-one-hole state $(2\pi 1h)$. The rate of the process is given by the first collision time $1/\tau_1$ and is determined by the corresponding Coulomb matrix elements or, in other words, by the available phase-space (the energy and the momentum must be conserved). The phase-space also determines in a crucial way the subsequent stages of the QP decay, which results in the creation of an increasing number of particles and holes, forming either localized or delocalized states in a Fock space. In the latter scenario the exponential decay is established after many generations of particles and holes have emerged. From these very general arguments it is obvious that the exponential decay requires a certain time to develop, which in our theory is determined by the parameter $\tau(\epsilon)$. This time parameter certainly exceeds the first collision time $\tau(\epsilon) > \tau_1$ obtained from the golden rule arguments applied to the bare Coulomb interaction (at the initial stages the screening is not efficient). This indicates that the time $\tau(\epsilon)$ cannot be obtained from either the bare nor the screened interaction and is distinct from the relaxation time at the large-time limit $(1/\gamma(\epsilon))$.

To obtain $\tau(\epsilon)$ let us recall the relations between the $n$th order spectral moments $M^{(n)}$ of the single-particle Green function and that of the self-energy $\Sigma^{(n)}$ (Ref. 8):

$$M^{(0)} = 1, \quad \delta\Sigma^{(0)} = M^{(1)} - \epsilon, \quad \Sigma^{(1)} = M^{(2)} - [M^{(1)}]^2.$$  

$\Sigma^{(0)} = \delta\Sigma^{(0)} + \Sigma^{(0)}_0$ is the frequency independent real part of the self-energy.\textsuperscript{19} These matrix relations directly follow from the Dyson equation, and can be obtained in any basis (Ref. 8 used a plane-waves basis). $\epsilon$ is a diagonal matrix with the elements given by the zeroth-order state energies (they already contain mean-field Coulomb interaction and, therefore, include $\Sigma^{(0)}_0$ (see Appendix B for exact definitions). For finite systems Hartree-Fock basis states seems to be appropriate. Writing the matrix of the spectral functions in terms of the imaginary part of the single-particle Green function ($A(\omega) = \frac{1}{\pi}\text{Im}G(\omega)$) and likewise for the spectral function of the self-energy ($S(\omega) = \frac{1}{\pi}\text{Im}\Sigma(\omega)$), and using the super-convergence theorem\textsuperscript{20} the matrices are cast as frequency integrals:

$$M^{(n)} = \int_{-\infty}^{\infty} d\omega \omega^n A(\omega), \quad n = 0 \ldots 2,$$

$$\Sigma^{(0)} = \int_{-\infty}^{\infty} d\omega S(\omega).$$

In HF basis $\delta\Sigma^{(n)}$ is rather small and is proportional to the difference of the direct and the exchange Coulomb energy computed with the Hartree-Fock and exact density matrix, i.e., related to the deviation of the natural occupations from 1 or 0. Thus, by virtue of Eqs. (8,10) we arrive at the conclusion that the Hartree-Fock energies in the first approximation are given by the center of mass of the spectral function. Likewise, by using Eqs. (9,10) we establish a formula for the matrix of standard deviations [cf. Eq. (1)]:

$$\sigma^2 = \int_{-\infty}^{\infty} d\omega S(\omega).$$

Its physical meaning in view of the relation (9) is the energy uncertainty of a many body-state. Formally an exact representation of this positively defined matrix can be written in terms of the six-point response function\textsuperscript{21} (Fig. 2a):

$$\Sigma(1, 1') - \Sigma(1, 1') = \int d(23) v(12) G(3^1, 12^1) v(21')$$

$$- \int d(2345) v(12) G(12, 2^15^1) G^{-1}(5, 4) G(42^1, 21') v(21')$$

$$\equiv \int d(23) v(12) G^{(3)}(3^1, 12^1) v(21'),$$

where $G(1 \ldots n, 1' \ldots n')$ denotes a general $n$-particle Green’s function, and $G^{(3)}(123, 1'2'3')$ stands for the irreducible $2p1h$ Green’s function. Its diagrammatic expansion in terms of the bare propagators is such that cutting a single fermionic line in each constituent diagram cannot separate the $2p1h$ entrance and exit channels.\textsuperscript{22} In Appendix A we sketch how the representation (13) can be derived from the equations of motion for the Green’s functions. In the present work, we compute the matrix standard deviations (12) for a finite system using different factorizations of $G^{(3)}$. Such unusual approach to generate approximations for the electron self-energy is motivated by the fact that the configuration interaction (CI) approach is capable of providing exact $n$-particle correlation functions in contrast to the ordinary many-body perturbation theory which tries to approach them by systematically summing up some classes of diagrams. We judge the accuracy of different approximations for the self-energy by comparing its zeroth spectral moment with exact value from full CI approach for a finite electron system.

**IV. NUMERICAL RESULTS**

As a prototypical system we consider the widely studied Na\textsuperscript{+} cluster.\textsuperscript{23} A small number of electrons makes it accessible to full CI.\textsuperscript{26} The $\sigma^2$ matrix can be computed exactly by exact diagonalization of the many-body Hamiltonian. We
use an algorithm by Olsen et al.\textsuperscript{28} based on the graphical unitary group approach\textsuperscript{29} for the generation of the restricted active space (RAS) and full CI Hamiltonians. The calculations are performed for each spin multiplicity separately using spin-adapted basis functions.\textsuperscript{30} In terms of the matrix elements of the creation and annihilation operators the spectral moments are expressed as

\[ M^{(n)} = \sum_{\rho}^{2N+1} \langle \rho | n \rangle X^n \bar{X}^\rho + \sum_{\rho \gamma} \langle \rho | Y^n \bar{Y}^\rho \rangle, \]  \hspace{1cm} (14)

where the summation is performed over the Hilbert space of the ionized states (dimension $D^{N+1}$) and electron attached states (dimension $D^{N+1}$). The matrix elements of electron creation ($\hat{a}_\alpha^\dagger$) and annihilation ($\hat{a}_\alpha$) operators

\[ X^\rho = \langle nN + 1| \hat{a}_\alpha^\dagger \hat{a}_\alpha | 0N \rangle, \quad Y^\rho = \langle qN - 1 | \hat{a}_\alpha^\dagger \hat{a}_\alpha | 0N \rangle, \]  \hspace{1cm} (15)

and the transition energies $\epsilon_\rho^+ = E_p^{N+1} - E_n^{N-1}, \epsilon_\rho^- = E_0^{N} - E_q^{N-1}$ are computed from the CI many-body states. Formally, for a finite system in a finite basis Eq. (15) yields non-diverging moments of any order. This is, however, an artifact of the numerical approach resulting from the truncation of the Hilbert space.

Approximations for the self-energy operator can be obtained from the factorization of the $2p1h$ six-points function\textsuperscript{19,21} (Fig. 2a). If the particle-hole ($p-h$) Green’s function is treated exactly we obtain the so-called GW approximation\textsuperscript{31} (Fig. 2b). Alternatively, this approximation can be obtained from the $\mathcal{W} = \mathcal{G} \mathcal{W}$ variational energy functional\textsuperscript{32} expanded in terms of the dressed electron propagator $\mathcal{G}$ and the screened Coulomb interaction $\mathcal{W}$. A single diagram of the first order has to be considered. Finally, one obtains the same functional form by neglecting the three-point vertex function $\Gamma$ in Hedin’s equations.\textsuperscript{33} It should be noted that we do not perform the self-consistent solution of Hedin’s equations; instead, we compute exactly $\mathcal{G}$ and $\mathcal{W}$ from the exact one-particle and particle-hole propagators. They are given by the Lehman representations in terms of many-body electron states.\textsuperscript{34,35} In accordance with the spectral representation of the self-energy\textsuperscript{26} we obtain for the energy-uncertainty:

\[ \Sigma^{(0),GW}_{\alpha \beta} = 4 \sum_{\rho \rho'} \sum_{\gamma \gamma'} \langle \alpha | n \rangle \langle n | \rho \rangle \langle \rho | \gamma \rangle \langle \gamma | \beta \rangle + (p-h)-h \text{ terms}, \]  \hspace{1cm} (16)

where we introduced a notation for the convolution of the Coulomb matrix elements $\langle \alpha \beta | \gamma \delta \rangle = \int d(r_1 r_2) \phi_\alpha^\dagger(r_1) \phi_\beta^\dagger(r_1) \phi_\gamma(r_2) \phi_\delta(r_2) / |r_1 - r_2|$, with matrix elements of the creation (or annihilation) operators [Eq. (15)] and with the density matrix elements $Q^\rho_{\gamma \delta} = \langle nN | \hat{a}_\alpha^\dagger \hat{a}_\beta | 0N \rangle$:

\[ \langle \alpha | p \rangle \langle n | \beta \rangle = \sum_{\gamma \delta} \langle \alpha | \gamma \rangle \langle \gamma | \beta \rangle Q^\rho_{\gamma \delta}. \]  \hspace{1cm} (17)

Analogically, one obtains an expression for the self-energy using the $(p-p)-h$ factorization (Fig. 2c):

\[ \Sigma^{(0),GW}_{\alpha \beta} = \sum_{\rho \rho'} \langle \alpha \beta | \gamma \delta \rangle Q^\rho_{\gamma \delta} = \sum_{\rho \rho'} \langle \alpha | n \rangle \langle n | \rho \rangle \langle \rho | \gamma \rangle \langle \gamma | \beta \rangle + (h-h)-p \text{ terms}, \]  \hspace{1cm} (18)

where similar to Eq. (17) we define the convolution of $(\alpha \beta | \gamma \delta)$ with the matrix elements of the two creation (annihilation) operators $P^m_{\gamma \delta} = \langle mN + 2 | \hat{a}_\gamma^\dagger \hat{a}_\delta^\dagger | 0N \rangle$:

\[ \langle \alpha | m \rangle = \sum_{\gamma \delta} \langle \alpha | \gamma \rangle \langle \gamma | \delta \rangle P^m_{\gamma \delta}. \]  \hspace{1cm} (19)

The $(p-p)-h$ factorization of the $2p1h$ Green’s function is nothing but the well known ladder-diagram expansion. Eqs. (16,18) can be thought of as the Fermi golden rule expressions. Since the delta-function ensuring the energy conservation is not present here the whole expression has a dimension of the energy squared. Starting from Eqs. (16,18) we further derive a series of simpler approximations. When the HF Green’s function is used in place of $\mathcal{G}$ we obtain the so-called $G^0W^0$ approximation. If, furthermore, the non-interacting excited states are used to compute $Q^\rho_{\gamma \delta}$ we obtain the $G^0W^0$ approximation with the spectral moment:

\[ \Sigma^{(0),GW}_{\alpha \beta} = 2 \sum_{n \gamma \delta} \langle \alpha | n \rangle \langle n | \gamma \rangle \langle \gamma | \delta \rangle n_s (1 - n_s), \]  \hspace{1cm} (20)

where $n_s$ is the occupation of the single-particle state $\gamma$. This is a rather simple and accurate approach as the comparison (Fig. 4) shows. Calculations on this level are feasible even for much larger systems (such as the C$_{60}$ fullerene\textsuperscript{36}).

For the Na$_6^+$ cluster we computed the spectral moments (Eqs. 14,16,18) by exact diagonalization of the many-body Hamiltonian. The details of CI calculations are presented in Tab. I. Comparison of CISDТ and CISDТQ calculation allows to estimate the accuracy of the former method to be in the range of $20$ meV which is sufficient for the present discussion. In what follows we only report the CISDT results.
The exact spectral function (solid line, Fig. 4a) of the lowest valence state ($e_{1 \text{HF}} = -9.786$ eV) is fragmented (two major peaks) and has multiple satellites. Despite this fact the model spectral function centered at the HF energy approaches the exact one in a large range of energies. The exact energy-uncertainty from the first two spectral moments of the spectral function (Eq. 14) is compared with the expressions resulting from the approximation (Eqs. 20,16,18) (Fig. 3). Corresponding self-energy spectral functions and weights are shown in Fig. 4(b,c). Generally, $GW$ weights are shown in Fig. 4(b,c). Generally, $GW$ self-energy yields results superior to other approximations studied here. Equally surprising is the large energy gap in the ladder approximation. It is possible, however, to relate this effect to the large magnitude of the second ionization potentials (last column of Tab. I). To make a quantitative statement we derive expressions for the gap in the self-energy spectrum as:

$$\Delta_{(p-h)-p} = E_{IP} - E_{EA} + 2\epsilon_1 = \Delta^N + 2\epsilon_1,$$

$$\Delta_{(p-p)-h} = E_{IP}^H - E_{EA}^H + E_{IP} - E_{EA} = \Delta^N + E_{IP}^H - E_{EA}^H,$$

where $\Delta^N$ is the quasiparticle gap. It is obvious now that the difference in gaps of the two self-energies arises due to the electron correlations: only for non-interacting systems the double energy of the first excited state equals to $E_{IP}^H - E_{EA}^H$, for the gapped system they typically lead to $E_{IP}^H - E_{EA}^H \gg 2\epsilon_1$. This is an extension to 2-particle case of a well known in quantum chemistry fact that $\Delta^N \gg \epsilon_1$ (positivity of the exciton and biexciton binding energies).

Despite the large deviation in energy positions and, therefore in the shape of the self-energy spectral function $S(\omega)$ (cf. solid and dash-dotted lines at Fig. 4(c)) the spectral moments are rather accurate and are close to those of $G_0W_0$ approximation. The latter approximation, albeit its simplicity, closely approaches the exact self-energy in the vicinity of the HOMOLUMO gap. For higher and lower energies the agreement, however, becomes poor and it confirms a well known fact that the satellite structures cannot be reproduced within this approach.\(^{37}\)

![FIG. 3. (Color online) Energy-uncertainty (Eq. 12) of the valence states of Na\(_9\) cluster computed at different levels of theory. Shaded area denotes deviation of the approximate theories from the exact.](image)

### TABLE I. Parameters of CI calculations for the Na\(_9\) cluster.

<table>
<thead>
<tr>
<th>$\kappa$</th>
<th>$D_0$</th>
<th>$D_{N-1}$</th>
<th>$D_{N-2}$</th>
<th>$\epsilon_1$</th>
<th>$E_{EA}$</th>
<th>$E_{IP}$</th>
<th>$E_{EA}^H$</th>
<th>$E_{IP}^H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>65</td>
<td>8</td>
<td>4</td>
<td>64</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>33</td>
<td>36</td>
<td>10</td>
<td>1.70</td>
<td>2.42</td>
<td>17.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>28</td>
<td>6</td>
<td></td>
<td>2.57</td>
<td>7.00</td>
<td></td>
<td></td>
<td>2.36</td>
</tr>
<tr>
<td>4</td>
<td>1425</td>
<td>376</td>
<td>180</td>
<td>1856</td>
<td>400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>561</td>
<td>708</td>
<td>170</td>
<td>2.02</td>
<td>2.41</td>
<td>17.49</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>264</td>
<td>132</td>
<td>2.14</td>
<td>7.32</td>
<td></td>
<td></td>
<td>2.38</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>924</td>
<td>198</td>
<td>2.96</td>
<td>17.28</td>
<td></td>
<td></td>
<td>2.91</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>12625</td>
<td>5640</td>
<td>2500</td>
<td>19776</td>
<td>3600</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4145</td>
<td>6336</td>
<td>1310</td>
<td>1.66</td>
<td>2.96</td>
<td>17.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3288</td>
<td>1524</td>
<td>2.75</td>
<td>6.94</td>
<td></td>
<td></td>
<td>2.91</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>9408</td>
<td>1746</td>
<td>2.77</td>
<td>6.92</td>
<td></td>
<td></td>
<td>2.91</td>
</tr>
</tbody>
</table>

### V. CONCLUSIONS

Summarizing, we presented a form of the quasiparticle line-shape that reflects the correct short and long time-limits of the single-particle Green function and, thus, can be used via, e.g. the generalized Kadanoff-Baym Ansatz,\(^{38,39}\) to parameterize evolving in time electronic structure (e. g., attosecond time-resolved photoemission). En route, we made some assumptions allow us to construct the spectral function physically valid in the whole energy range with the correct asymptotic behavior. These are: for a given particle-hole excitation the spectral function is represented by a single peak positioned at the mean-field energy having the strength exactly equal to one to ensure the normalization. In contrast, in the theory of Fermi liquids one is focused in a small interval of energies around the quasiparticle peak (shifted from the mean-field position) where the shape is essentially Lorentzian with a smooth incoherent background. If even a more accurate description of the peak is desired the asymmetric Breit-Wigner form can be derived.\(^{40}\) This, however, further reduces the admissible range of energies as already in the vicinity of the peak the spectral density becomes negative. Our interpolative for-
mula certainly misses such detailed structure in the energy domain having more emphasis on the time-evolution.

The main ingredient of our approach is the energy uncertainty \( \sigma^2(\epsilon) \) of many-body states. The CI method enables us to compute it either exactly or by a number of diagrammatic approximations. Such calculations, besides providing an input for the description of the state’s time evolution, also give a measure of the approximations’ actual accuracy. Our simulations indicate that for the system considered here rather accurate results are obtained by neglecting the three-particle correlations. Among the possible decoupling schemes: the GW approach ((p-h)-p) and the ladder approximation ((p-p)-h) the former gives more accurate results, although this might not hold in general. Regarding experiments measuring the initial time of the decay, we note that that this decay will generally quadratic in time. The important quantity however is the decay constant \( \sigma \) which can be easily extracted experimentally from the initial time evolution. As evident from Fig. 3 various levels of approximation and/or different contributing processes lead to a different \( \sigma \) that can be considered as the material-dependent quantity to be determined in an attosecond time-resolved experiment for the decaying excitations.

VI. ACKNOWLEDGMENTS

The work is supported by DFG-SFB762 [YP, JB]. AR acknowledge financial support from the European Research Council Advanced Grant DYNamo (ERC-2010-AdG – Proposal No. 267374), Spanish Grants (FIS2011-65702 C02-01 and PIB2010US-00652), ACI-Promocion (ACI2009-1036), Grupos Consolidado UPV/EHU del Gobierno Vasco (IT-319-07) and European Commission projects CRONOS (280879-2 CRONOS CP-FP7) and THEMA (FP7-NMP-2008-SMALL-2, 228539). Computational time was granted by i2basque and BSC Red Española de Supercomputación.

Appendix A: Properties of the spectral function

a. Definitions: We can start from the Lehmann representation:

\[
G_{ij}(\omega) = \sum_{\mu \in \Delta^{N+1}} \frac{\mathcal{R}_{\mu ij}^+}{\omega - \epsilon_\mu^+ + i\eta} + \sum_{\mu \in \Delta^{N-1}} \frac{\mathcal{R}_{\mu ij}^-}{\omega - \epsilon_\mu^- - i\eta},
\]

where

\[
\epsilon_\mu^+ = E_{\mu}^{(N+1)} - E_0^{(N)} \geq -E_{EA}, \quad \epsilon_\mu^- = E_0^{(N)} - E_{\mu}^{(N-1)} \leq -E_{IP}.
\]

In terms of previously introduced matrix elements [Eq. (15)] the residues of the Green’s function are given by:

\[
A_{\mu ij}^+ = \langle 0(N|\hat{a}_i|\mu N + 1)\langle \mu N + 1|\hat{a}_j^+|0N\rangle, \quad \text{and}
A_{\mu ij}^- = \langle 0(N|\hat{a}_i^+|\mu N - 1)\langle \mu N - 1|\hat{a}_j|0N\rangle.
\]

We apply the identity

\[
\frac{1}{x \pm i\eta} = \mathcal{P} \frac{1}{x} \mp i\eta \delta(x)
\]

and obtain:

\[
\frac{1}{\pi} \text{Im} G_{ij}(\omega) = -\sum_{\mu \in \Delta^{N+1}} \mathcal{R}_{\mu ij}^+ \delta(\omega - \epsilon_\mu^+) + \sum_{\mu \in \Delta^{N-1}} \mathcal{R}_{\mu ij}^- \delta(\omega - \epsilon_\mu^-).
\]

Typically, and we will always assume it, there is a well defined Fermi level \( \epsilon_F \) located somewhere between the negative of the ionization potential \( -E_{HOMO} \) and of the electron affinity \( -E_{LUMO} \):

\[
\epsilon_\mu^- \leq -E_{IP} \leq \epsilon_F \leq -E_{EA} \leq \epsilon_\mu^+.
\]

In fact, some examples to demonstrate a possibility of \( -E_{EA} < -E_{IP} \) have been constructed.11 There, the authors consider the density functional theory with continuous number of electrons \( N \) and construct the total energy which is concave as a function of \( N \). This implies the negative hardness \( \eta \) defined as:

\[
\eta = \frac{1}{2} \left. \frac{\partial^2 E}{\partial N^2} \right|_{N=N_0} \geq \frac{E_{IP} - E_{EA}}{2}.
\]
For the usual case (A3) we can introduce the spectral representation:

\[ \mathcal{G}_{ij}(\omega) = \int_{\omega - \omega'} S_{ij}(\omega') d\omega', \]

where the contour runs infinitesimally close from above to the real axis for energies below the Fermi energy and below the real axis for energies above the Fermi energy (see Fig. 3 of Ref. 42). It follows then

\[ S_{ij}(\omega) = \sum_{p=2D} \tilde{A}_{p} \delta(\omega - \epsilon_{p}) + \sum_{p=2D'} \tilde{A}_{p} \delta(\omega - \epsilon'_{p}) = \pm \frac{1}{\pi} \text{Im} \mathcal{G}_{ij}(\omega), \]

where (+) stands for \( \omega < \epsilon_{F} \) and (−) for \( \omega > \epsilon_{F} \). From the last expression Eq. (14) trivially follows.

b. Relation between properties of \( \mathcal{G} \) and \( S \) at small times:

It is reasonable to assume the following general expansion of the electron Green’s function

\[ \mathcal{G}_{k}(t) = \mathcal{G}_{k}^{0}(t) \sum_{n} a_{n}(it)^{n}. \]

This can most naturally come from the cumulant expansion. What is the corresponding spectral function? In the \( \omega \)-space it is given by:

\[ S_{k}(\omega) = \sum_{n} a_{n} \delta^{(n)}(\omega - \epsilon_{k}), \]

where \( \delta^{(n)}(\omega) \) formally denotes the \( n \)th derivative of the \( \delta \)-function. Henceforth, after the Fourier transform we obtain:

\[ S_{k}(t) = \sum_{n} a_{n} \int \frac{d\omega}{2\pi} e^{-i\omega t} \delta^{(n)}(\omega - \epsilon_{k}) = \sum_{n} a_{n}(it)^{n}. \]

Appendix B: Derivation of the self-energy representation in terms of 2\( p \)-1\( h \) irreducible Green’s function

We start with the equations of motion for the general one and two-particle Green’s function. We do not specify from the beginning what channel \( p-h \) or \( p-p \) do we consider. It will be clear later when we introduce a specific ordering of the time arguments.

\[ \mathcal{G}(1, 1') = \mathcal{G}^{0}(1, 1') - i \int d(23) \mathcal{G}^{0}(1, 2) \nu(23) \mathcal{G}(23, 3^+ 1'), \]

with \( (i) \equiv (r_{i}, s_{i}, t_{i}) \) and \( (i^+) \equiv (r_{i} + \delta, s_{i}, t_{i} + \delta), \ \delta > 0. \) (B1)

By comparing with the Dyson equation we see that the self-energy can be written in terms of the two-particle Green’s function:

\[ \Sigma(1, 1') = -i \int d(23) \nu(13) \mathcal{G}(13, 3^+ 2) \mathcal{G}^{-1}(2'). \] (B2)

Thus, we will try to express the self-energy in terms of a higher order correlation function:

\[ \mathcal{G}(12, 1'2') = \mathcal{G}^{0}(1, 2') \mathcal{G}(2, 1') - \mathcal{G}^{0}(1, 1') \mathcal{G}(2, 2') - i \int d(34) \mathcal{G}^{0}(1, 3) \mathcal{G}(34, 1'2'4^+). \] (B3)

However, we must eliminate \( \mathcal{G}^{0} \) from (B3). To do so we take the inverse of (B1):

\[ [\mathcal{G}^{-1}(1, 1')^{-1}(1, 1')^{-1} = \mathcal{G}^{-1}(1, 1') - i \int d(23) \nu(12) \mathcal{G}(12, 2'3) \mathcal{G}^{-1}(3, 1'), \] (B4)

multiply (B3) with \( \mathcal{G}(6, 5)[\mathcal{G}^{0}]^{-1}(5, 1) \) on the left (the side actually is not important as the functions are commutative) and integrate:

\[ \int d(51) \mathcal{G}(6, 5)[\mathcal{G}^{0}]^{-1}(5, 1) \mathcal{G}(12, 1'2') = \mathcal{G}(6, 2') \mathcal{G}(2, 1') - \mathcal{G}(6, 1') \mathcal{G}(2, 2') \]

\[ - i \int d(34) \mathcal{G}(6, 3) \nu(34) \mathcal{G}(324, 1'2'4^+), \] (B5)

and finally use (B4) on the lefthand side of (B5). A rather long expression follows:

\[ \mathcal{G}(62, 1'2') - i \int d(7341) \mathcal{G}(6, 3) \nu(34) \mathcal{G}(34, 4^+ 7) \times \mathcal{G}^{-1}(7, 1) \mathcal{G}(12, 1'2') = \mathcal{G}(6, 2') \mathcal{G}(2, 1') - \mathcal{G}(6, 1') \mathcal{G}(2, 2') \]

\[ - i \int d(34) \mathcal{G}(6, 3) \nu(34) \mathcal{G}(324, 1'2'4^+). \] (B6)

Here we introduce the irreducible function \( \mathcal{G}^{(3)} \) according to:

\[ \mathcal{G}^{(3)}(123, 1'2'3') = \mathcal{G}(123, 1'2'3') \]

\[ - \int d(45) \mathcal{G}(13, 3'4) \mathcal{G}^{-1}(4, 5) \mathcal{G}(52, 1'2') \] (B7)

and write after the reordering of variables:

\[ \mathcal{G}(12, 1'2') = \mathcal{G}(1, 2') \mathcal{G}(2, 1') - \mathcal{G}(1, 1') \mathcal{G}(2, 2') \]

\[ - i \int d(34) \mathcal{G}(1, 3) \nu(34) \mathcal{G}^{(3)}(324, 1'2'4^+). \] (B8)

Now we can substitute it in the definition (B2). After trivial, but lengthy manipulation we obtain:

\[ \Sigma(1, 1') = \delta(11') \int d(3) \nu(3) \mathcal{G}(13) - \nu(11') \mathcal{G}(11') \]

\[ + \int d(36) \nu(13) \mathcal{G}^{(3)}(6'13, 63^+ 1') \mathcal{G}(61'). \] (B9)

The first term here is just the direct interaction with the usual definition of the density \( n(1) = -i \mathcal{G}(1, 1') \). The second term is the exchange interaction with the density matrix defined as \( n(1') = -i \mathcal{G}(1, 1') \). These two terms are included in the mean-field Hamiltonian \( H(1, 1') = \delta(11') \mathcal{T}(1) + \mathcal{V}(1) + \Sigma^{(0)}(11') \) and therefore are excluded from otherwise identical equation (13). The summation over the spin variables (included in the definition of the integrals) leads to the appearing of the prefactor 2 in the direct term for closed shell systems. The exact frequency independent part of the self-energy is given by:

\[ \Sigma^{(0)}(11') = \delta(11') \int d(3) \nu(3) \mathcal{G}(13) - \nu(11') \mathcal{G}(11'), \]
whereas in the mean-field Hamiltonian $\Sigma_0(1')$ is computed by the same formula from the zeroth order densities, i.e. $\rho_0(1') = -iG_0(1, 1')$. 

---

16. A typical approach to establish the positivity of a Fourier transform is to use the convexity of the function. Obviously, in our case the function is not convex everywhere, but this can be circumvented by shifting the contour of integration to the region where this condition is fulfilled.
39. T. Kita, Progress of Theoretical Physics, 123, 581 (2010).