Supplementary Material

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FUNCTIONAL DERIVATION OF GW+EDMFT

We consider the action formalism, in which consistent approximations can be derived from a common functional [1] and in which the generalization to real time dynamics is easily obtained by the Baym-Kadanoff formalism. The general strategy is to construct a Baym-Kadanoff functional Γ by a Legendre transform of the free energy Ω. The free energy Ω is a functional of the bare propagator G_0 and the interaction v, $\Omega \equiv \Omega[G_0, v]$. By the Legendre transform the functional dependence is changed, making Γ (except for the Hartree part $\Gamma^{\rm H}$) a functional of the (interacting) single particle Green's function $G_{ij}(t,t') = -i\langle T_{\mathcal{C}} c_i(t) c_j^*(t')\rangle$ and the screened interaction $W_{ij}(t,t')$, $\Gamma \equiv \Gamma[G,W]$. At the physical G and W the Legendre transform guarantees that Γ is stationary and takes the value of the free energy Ω. Via a suitable Hubbard-Stratonovich (HS) transformation [2, 3] the screened interaction $W_{ij}(t,t')$ can be shown to be related to the charge susceptibility $\chi_{ij}(t,t') = -i\langle T_{\mathcal{C}} \tilde{n}_i(t)\tilde{n}_j(t')\rangle$ through the integral relation

$$W = v + v * \chi * v, \tag{S.1}$$

where the $*$-product denotes a convolution on the Baym-Kadanoff L-shaped time-contour and a sum over (adjacent) real space indices. The HS transformation yields a scalar electron-boson vertex α equal to unity, $\alpha = 1$, however, in the functional treatment it is convenient to also consider the $\alpha = 0$ case, where the electron and boson systems are decoupled.

The Baym-Kadanoff functional Γ can be written as

$$\Gamma_{\alpha=1}[G,W] = \Gamma_{\alpha=0}[G,W] + \Gamma^{\rm H}[G,v] + \Psi[G,W], \tag{S.2}$$

where $\Gamma_{\alpha=0}$ is the decoupled part of Γ,

$$\begin{aligned}\Gamma_{\alpha=0} = {} & \mathrm{Tr}[\ln(-G)] - \mathrm{Tr}[G_0^{-1} * G] \\ & - \frac{1}{2}\mathrm{Tr}[\ln(W)] + \frac{1}{2}\mathrm{Tr}[v^{-1} * W].\end{aligned} \tag{S.3}$$

The Hartree contribution to the functional, $\Gamma^{\rm H} = -2\frac{i}{2}\mathrm{Tr}[G_{ii}(t,t^+)v_{ij}G_{jj}(t,t^+)]$, only depends on the bare interaction and has to be treated separately. The factor of 2 originates from the sum over spin degrees of freedom. The remaining many-body complexity of the system is now captured by the Almbladh functional $\Psi \equiv \Psi[G,W]$, comprising all possible two-particle irreducible diagrams built with the G and W propagators [4]. The physical solution corresponds to the stationary points of the Baym-Kadanoff functional Γ with respect to G and W, namely $\frac{\delta\Gamma}{\delta G} = 0$ and $\frac{\delta\Gamma}{\delta W} = 0$, which yields the Dyson equations for G and W:

$$G^{-1} = G_0^{-1} - \Sigma^{\rm H} - \Sigma^{\rm xc}, \qquad W^{-1} = v^{-1} - \Pi, \tag{S.4}$$

wherein $\Sigma^{\rm H} = \delta_G\Gamma^{\rm H}[G,v]$ is the Hartree self energy, and the exchange-correlation self energy $\Sigma^{\rm xc}$ and the polarization Π are obtained from variations of the Almbladh functional Ψ,

$$\Sigma^{\rm xc} = \frac{\delta\Psi}{\delta G}, \qquad \Pi = -2\frac{\delta\Psi}{\delta W}. \tag{S.5}$$

Evaluating all diagrams in Ψ is not a tractable problem, and therefore we seek approximations that keep only a subset of the diagrams. GW is such an approximation, which retains only the lowest order contribution in the electron-boson coupling α (apart from the Hartree term, which is treated separately). It corresponds to the following approximation of the Almbladh functional:

$$\Psi \approx \Psi_{GW} \equiv \frac{i}{2}\mathrm{Tr}[G_{ij}(t,t')W_{ij}(t,t')G_{ji}(t',t)]. \tag{S.6}$$

The resulting approximations for the self energy, $\Sigma^{GW}_{ij}(t,t') = iG_{ij}(t,t')W_{ij}(t,t')$, and polarization, $\Pi^{GW}_{ij}(t,t') = -iG(t,t')_{ij}G(t',t)_{ji}$, provide a decent description of weakly correlated systems and capture charge fluctuation driven nonlocal physics, like screening, plasmonic collective modes, and charge density waves. However, as a weak coupling expansion, it fails to describe effects of strong correlations, like Mott's metal-insulator transition.

An approximation that captures these latter phenomena is extended dynamical mean field theory (EDMFT), which corresponds to the following local approximation of the Almbladh functional:

$$\Psi \equiv \Psi[G_{ij}, W_{ij}] \approx \Psi[G_{ii}, W_{ii}] \equiv \Psi_{\rm EDMFT}. \tag{S.7}$$

Note that this is a highly non-perturbative approximation that accounts for all diagrams, which contain only local propagators.

In order to capture both the effect of strong interactions and nonlocal physics we can combine the two functionals [5], by supplementing the local diagrams in $\Psi_{\rm EDMFT}$ with all nonlocal GW diagrams,

$$\begin{aligned}\Psi \approx \Psi_{GW+\rm EDMFT} \equiv {} & \Psi_{\rm EDMFT}[G_{ii}, W_{ii}] \\ & + \Psi_{GW}[G_{ij}, W_{ij}] - \Psi_{GW}[G_{ii}, W_{ii}],\end{aligned} \tag{S.8}$$

arriving at the GW+EDMFT approximation of the Almbladh functional $\Psi_{GW+\rm EDMFT}$.

The basic insight of the EDMFT approach is the observation that there exists a solvable many-body problem, whose Almbladh functional is given by $\Psi_{\rm EDMFT}[G_{ii}, W_{ii}]$, namely an effective impurity problem (for the simpler DMFT case see Ref. 6). In order to evaluate the self-energy contributions from $\Psi_{\rm EDMFT}[G_{ii}, W_{ii}]$ we want to construct this impurity system so that it has the local Green's function G_{ii} and screened interaction W_{ii} of the lattice problem. This is achieved by deriving constraining equations for the *a priori* unknown impurity Weiss field $\mathcal{G}$ and effective impurity interaction $\mathcal{U}$. The Baym-Kadanoff functional Γ' of the impurity problem can be expressed as

$$\Gamma' = \Gamma'_0 + \Gamma^{\rm H\prime} + \Psi_{\rm EDMFT}[G_{ii}, W_{ii}], \tag{S.9}$$

where the decoupled contribution is

$$\begin{aligned}\Gamma'_0 =& \,{\rm Tr}[\ln(-G_{ii})] - {\rm Tr}[\mathcal{G}^{-1} * G_{ii}] \\ &- \frac{1}{2}\,{\rm Tr}[\ln(W_{ii})] + \frac{1}{2}\,{\rm Tr}[\mathcal{U}^{-1} * W_{ii}],\end{aligned} \tag{S.10}$$

and the Hartree contribution is given by

$$\Gamma^{\rm H\prime} = -2\tfrac{i}{2}\,{\rm Tr}[G_{ii}(t,t^+)\mathcal{U}(t,t')G_{ii}(t',t'^+)]. \tag{S.11}$$

Demanding that the lattice system functional Γ and the impurity system functional Γ' have the same local G_{ii} and W_{ii} causes both functionals to be stationary ($\delta_{G_{ii}}\Gamma' = 0 = \delta_{G_{ij}}\Gamma$ and $\delta_{W_{ii}}\Gamma' = 0 = \delta_{W_{ij}}\Gamma$ or, for convenience [6], $\delta_{G_{ii}}(\Gamma - \Gamma') = \delta_{G_{ii}}\Gamma_{GW+\rm EDMFT} = 0$, $\delta_{W_{ii}}(\Gamma - \Gamma') = \delta_{W_{ii}}\Gamma_{GW+\rm EDMFT} = 0$), which yields the conditions for the auxiliary quantities $\mathcal{G}$ and $\mathcal{U}$ that will have to be satisfied by the selfconsistent solution. We have the following explicit expressions:

$$\begin{aligned}\frac{\delta\Gamma_{GW+\rm EDMFT}}{\delta G_{ii}} =& -[G_0^{-1}]_{ii} + [G^{-1}]_{ii} + \mathcal{G}^{-1} - [G_{ii}]^{-1} \\ &+ \Sigma^{\rm H} - \Sigma^{\rm H\prime} = 0, \\ \Rightarrow \mathcal{G}^{-1} =& \,[G_{ii}]^{-1} + \Sigma^{\rm xc}_{ii} + \Sigma^{\rm H\prime},\end{aligned} \tag{S.12}$$

$$\begin{aligned}&\frac{\delta\Gamma_{GW+\rm EDMFT}}{\delta W_{ii}} = [v^{-1}]_{ii} - [W^{-1}]_{ii} - \left(\mathcal{U}^{-1} - [W_{ii}]^{-1}\right) = 0, \\ &\Rightarrow \mathcal{U}^{-1} = [W_{ii}]^{-1} + \Pi_{ii}.\end{aligned} \tag{S.13}$$

Equations (S.12) and (S.13) constitute the self-consistency condition for the GW+EDMFT approach.

The final Dyson equations of the lattice system in the GW+EDMFT approximation thus read

$$[G_0^{-1}]_{ij} - [G^{-1}]_{ij} = \Sigma^H_{ij} + \delta_{ij}\Sigma^{\rm xc}_{ii} + (1-\delta_{ij})\Sigma^{GW}_{ij}, \tag{S.14}$$

$$[v^{-1}]_{ij} - [W^{-1}]_{ij} = \delta_{ij}\Pi_{ii} + (1-\delta_{ij})\Pi^{GW}_{ij}, \tag{S.15}$$

where $\Sigma^{\rm xc}_{ii}$ and Π_{ii} are obtained from Eqs. (S.12) and (S.13).

In the actual implementation the self-energy contributions are grouped slightly differently to take advantage of the Hartree and Fock self-energy contribution $\Sigma^{\rm HF}$ being instantaneous

$$\begin{aligned}\Sigma^{GW+\rm EDMFT}_k =& \Sigma^{\rm HF}_k + \Sigma^{GW_c,\rm nl}_k + \Sigma^{\rm xc}_{ii} \\ =& [\Sigma^{\rm HF}_k + \Sigma^{\rm H\prime}] + \Sigma^{GW_c,\rm nl}_k + \\ & [\Sigma^{\rm xc}_{ii} - \Sigma^{\rm H\prime}],\end{aligned} \tag{S.16}$$

where $\Sigma^{GW_c,\rm nl} = \Sigma^{GW_c}_k - \sum_k \Sigma^{GW_c}_k$ is the nonlocal part and $\Sigma^{GW_c}_{ij}(t,t') = iG_{ij}(t,t')(W_{ij} - v_{ij})(t,t')$ is the GW self-energy with the Fock term removed.

The last bracket on the right hand side follows naturally when the combined weak-coupling and hybridization expansion is performed in terms of the density fluctuations $\tilde{n} = n - \langle n\rangle$ instead of the density [7, 8]:

$$\begin{aligned}&\frac{1}{2}\int\int dtdt'\tilde{n}(t)\mathcal{U}(t,t')\tilde{n}(t') = \frac{1}{2}\int\int dtdt' n(t)\mathcal{U}(t,t')n(t') \\ &- \langle n\rangle\int dtdt'\mathcal{U}(t,t')n(t') + \langle n\rangle\langle n\rangle\int dtdt'\mathcal{U}(t,t').\end{aligned} \tag{S.17}$$

Then, the second term on the r.h.s. cancels the impurity Hartree contribution $\Sigma^{\rm H'}(t,t') = \delta_{\mathcal{C}}(t,t')\langle n\rangle\int d\bar{t}\mathcal{U}(t,\bar{t})$, where $\delta_{\mathcal{C}}$ marks the Delta function on the Baym-Kadanoff contour.

THEORETICAL DESCRIPTION OF TIME-RESOLVED ELECTRON ENERGY LOSS SPECTROSCOPY

Here we give details on the theoretical description of the time-resolved electron energy loss spectroscopy (EELS). We will combine the equilibrium analysis of the EELS cross section as described in Ref. 9 and a generalization of the photoemission spectroscopy to the non-equilibrium case [10, 11]. In an EELS experiment the sample is probed with a pulse of electrons with definite wave-vector and energy $|k_1, E_1\rangle$, which is scattered to some final state $|k_2, E_2\rangle$. The resolved signal is proportional to the total number of electrons per solid angle $d\Omega_{k_2}$ and energy interval dE_2,

$$I_{k_1}(k_2) = \frac{dN(k_2)}{d\Omega_{k_2}dE_2}, \tag{S.18}$$

that are emitted from the sample.

The initial state at some early time t_i is given by the thermal ensemble of the many-body states $|\Phi_n\rangle$ in the crystal at the temperature T with the density matrix $\rho(t_i) = \mathcal{Z}^{-1}\sum_n \exp[-\mathcal{E}_n(t_i)/T]|\Phi_n\rangle \otimes |k_1, E_1\rangle\langle k_1, E_1| \otimes \langle\Phi_n|$, where the $\mathcal{E}_n$ are the energy eigenvalues, and the free probe electrons are denoted by $|k_1, E_1\rangle$. This initial ensemble $\rho(t_i)$ is evolved to some later time t, $\rho(t) = U(t,t_i)\rho(t_i)U(t_i,t)$, via the unitary time evolution operator $U(t,t') = \mathcal{T}\exp[-i\int_{t'}^{t} d\bar{t}(H(\bar{t}) + H_{\rm probe}(\bar{t}))]$, where $\mathcal{T}$ is the time ordering operator. The lattice system, including the pump pulse, is described by the $H(t)$ given in Eq. (1) of

the main text and the probe electrons interact with the solid via a density-density interaction with transfers of momenta $q = k_2 - k_1$ and energy $\omega = E_2 - E_1$,

$$H_{\text{probe}} = \sum_{k,k_1,q} s(t) e^{-i\omega t} M_q(k_1) c^\dagger_{k-q} c_k b^\dagger_{k_1+q} b_{k_1}, \quad \text{(S.19)}$$

where b_k ($b^\dagger_k$) annihilates (creates) a probe electron with energy E_k and momentum k, $s(t)$ is the envelope of the probe pulse at the sample (peaked around t_p) and $M_q(k_1)$ is the matrix element for the scattering. In the case of EELS the matrix element is proportional to the Coulomb interaction V_q within the plane $M_q(k_1) \propto V_q$, see the discussion in Ref. 9. In this treatment the exchange interaction between the probe electrons and electrons in the solid is neglected as well as the presence of the surface, namely we assume that the probe-electrons measure bulk-properties of the system and that matrix elements satisfy the conservation of momentum in the plane. These simplifications can be lifted, and do not alter the general structure of the time resolved EELS response, see Ref. 9 for a thorough discussion.

The number of the detected electrons after the scattering at time t_f is given by

$$N(k_2, t_f) = \text{Tr}[n^b_{k_2} \rho(t_f)] \quad \text{(S.20)}$$

and the leading contribution to the measured number of electrons is given by the second-order time-dependent perturbation theory in the probe Hamiltonian $H_{\text{probe}}(t)$ [10]

$$\begin{aligned} N(k_2, t_f) = &\iint_{t_i}^{t_f} dt dt' \, \text{Tr}[U_0(t_i, t') H_{\text{probe}}(t') \\ &\times U_0(t', t_f) n^b_{k_2} U_0(t_f, t) H_{\text{probe}}(t) U_0(t, t_i) \rho(t_i)], \end{aligned} \quad \text{(S.21)}$$

where $U_0(t, t')$ is the time evolution operator of the system without probe-system coupling, $U_0(t, t') = \mathcal{T} \exp[-i \int_{t'}^{t} d\bar{t} H(\bar{t})]$. The evaluation of the expectation value leads to the expression for the time-resolved EELS signal,

$$\begin{aligned} &I_{k_1}(k_2 = k_1 + q) \propto |M_q(k_1)|^2 I_{q,\omega} \\ &I_{q,\omega} = \iint_{-\infty}^{\infty} dt dt' s(t) s(t') e^{i\omega(t-t')} i\chi^<_q(t, t'), \end{aligned} \quad \text{(S.22)}$$

where we sent the initial and final time to plus/minus infinity without lack of generality, $t_f, t_i \to +\infty, -\infty$, and $\chi_q(t, t') = -i\langle T_{\mathcal{C}} n_q(t) n_{-q}(t') \rangle$ is the momentum-dependent density-density response function of the sample (whose lesser component is defined as $i\chi^<_q(t', t) = \langle n_{-q}(t) n_q(t') \rangle$). We note in passing that Eq. (S.22) is positive definite by construction.

First we will show that in equilibrium Eq. (S.22) reduces to the conventional expression for the EELS cross-section in terms of $\text{Im}[\chi^R(\omega)]$ [2, 9]. The response of the equilibrium state is time translation invariant, $\chi^<_q(t', t) = \chi^<_q(t' - t)$ so when assuming a long probe electron envelope ($s(t) =$ const.), Eq. (S.22) reduces to $i\chi^<_q(-\omega)$. The lesser component can be related to the retarded component through the fluctuation dissipation theorem, $i\chi^<_q(\omega) = -2 f_B(\omega) \text{Im}[\chi^R_q(\omega)]$, where $f_B(\omega)$ is the Bose distribution function. The retarded component is odd with respect to frequency $\text{Im}[\chi^R_q(\omega)] = -\text{Im}[\chi^R_q(-\omega)]$. Thus, for frequencies larger than the temperature $|\omega| \gg 1/\beta$, where the Bose distribution function can be approximated with a Heaviside function $f_B(\omega) \approx -\theta(-\omega)$, we have

$$I_{q,\omega} \propto i\chi^<_q(-\omega) \approx -2\theta(\omega) \text{Im}[\chi^R_q(\omega)]. \quad \text{(S.23)}$$

In other words, in this limit there is only energy loss ($\omega > 0$), and the EELS cross-section is given by the spectral density of the valence electron density-density response function.

Out of equilibrium, the convolution with the probe envelopes $s(t)$ can be viewed as a filter for the susceptibility $\chi^<_q(t, t')$ in the time-frequency plane, similar to the case of photoemission spectroscopy [12]. In the simplest approximation, we assume a Gaussian wave packet $s(t) \propto e^{-(t-t_p)^2/2\delta t^2}$ of duration δt centered around a probe time t_p. Then Eq. (S.22) becomes the convolution of the Wigner transform

$$\chi^<_q(t, \omega) = \int_{-\infty}^{\infty} ds \, e^{i\omega s} \chi^<_q(t + s/2, t - s/2)$$

with a Gaussian kernel of width δt and $\delta\omega = 1/\delta t$ centered at frequency $-\omega$ and time t_p. As in the case of photoemission spectroscopy, if the evolution of the spectrum is fast compared to the inverse width of relevant spectral signatures, the form of the spectrum will strongly depend on the time-profile $s(t)$ of the probe pulse [12]. In the present paper, however, we characterize the spectrum of the system on the frequency scale of the order of the bandwidth, in a non-thermal steady state that lives much longer than the inverse bandwidth. In such a non-thermal quasi-steady state we can approximate $I_{q,\omega}$ by the Wigner transform [13],

$$I_{q,\omega} \propto i\chi^<_q(t_p, -\omega). \quad \text{(S.24)}$$

This is the approximation for the EELS cross-section employed in this paper.

In general, there will be both energy loss and gain, as described by the signal $I_{q,\omega}$ at positive and negative frequencies, respectively. In both cases, the result given by Eq. (S.22) is positive definite. To detect the population inversion experimentally, one can evaluate the *difference* $\Delta I_{q,\omega}$ between the gain and the loss,

$$\begin{aligned} \Delta I_{q,\omega} &= I_{q,\omega} - I_{q,-\omega} \propto \iint_{-\infty}^{\infty} dt dt' \, s(t) s(t') \\ &\times \left[e^{i\omega(t-t')} \langle n_{-q}(t) n_q(t') \rangle - e^{-i\omega(t-t')} \langle n_{-q}(t) n_q(t') \rangle \right] \\ &= \iint_{-\infty}^{\infty} dt dt' \, s(t) s(t') e^{i\omega(t-t')} i[\chi^<_q(t', t) - \chi^>_q(t', t)] \\ &= 2\text{Im} \iint_{-\infty}^{\infty} dt dt' s(t) s(t') e^{i\omega(t-t')} \chi^R_q(t', t), \end{aligned} \quad \text{(S.25)}$$

defined for positive frequencies $\omega > 0$. In the third line of Eq. (S.25) we have relabeled the time arguments $t \leftrightarrow t'$ in the second term under the integral, and assumed momentum inversion symmetry $\chi_q(t,t') = \chi_{-q}(t,t')$], while in the fourth line we have used the anti-hermiticity relation $\chi_q^{>,<}(t,t') = -\chi_q^{>,<}(t',t)^*$. In the quasi-steady state we employ the same approximation as in Eq. (S.24), and obtain the difference between the EELS energy-gain and energy-loss cross section as

$$\Delta I_{q,\omega} \approx 2\mathrm{Im}\chi_q^R(t,-\omega) = -2\mathrm{Im}\chi_q^R(t,\omega), \tag{S.26}$$

which lead to the EELS signal

$$I_{k_1}(k_2 = k_1 + q) \propto V_q^2 \mathrm{Im}\chi_q^R(t,\omega). \tag{S.27}$$

Hence the *difference in energy gain and energy loss* at energy ω can be used to detect the transient population-inversion in the density fluctuations of the system. In Fig. 4 of the main text we plot the related quantity $V_q \mathrm{Im}\chi_q^R(t,\omega)$, which corresponds to the inverse dielectric constant.

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[13] In fact, any Fourier transform with respect to a time-difference is equivalent in a steady state, up to a phase factor.