Thermodynamic Stability at the Two-Particle Level

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We show how the stability conditions for a system of interacting fermions that conventionally involve variations of thermodynamic potentials can be rewritten in terms of one- and two-particle correlators. We illustrate the applicability of this alternative formulation in a multiorbital model of strongly correlated electrons at finite temperatures, inspecting the lowest eigenvalues of the generalized local charge susceptibility in proximity of the phase-separation region. Additionally to the conventional unstable branches, we address unstable solutions possessing a positive, rather than negative, compressibility. Our stability conditions require no derivative of free-energy functions with conceptual and practical advantages for actual calculations and offer a clear-cut criterion for analyzing the thermodynamics of correlated complex systems.

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Introduction—Thermodynamic stability is a crucial concept for condensed matter systems. The conventional formulation of stability criteria relies on derivatives of thermodynamic potentials, i.e., on the Hessian matrix of the grand potential Ω, taken with respect to the independent variables considered, such as temperature, volume, and chemical potential. In the textbook example of the liquid-gas transition [1], the stability of the Van der Waals isotherms in the pressure-versus-volume plane can be directly inspected by calculating the isothermal compressibility, which can be expressed with the second derivative of the grand potential with respect to the volume. Similar considerations extend also to many-electron systems in the presence of a local Coulomb interaction. The latter induces metal-to-Mott insulator transitions at finite doping, close to which two derivatives are needed in order to set the stability conditions at a fixed temperature: one with respect to the strength of the Hubbard repulsion and one with respect to the chemical potential [2–6]. The dimension of the Hessian matrix would further increase as one keeps adding thermodynamic variables, hence leading to a higher number of independent derivatives to be considered. One can therefore ask whether it is possible to encode the same information in a single "local" state variable, whose very value diagnoses the thermodynamic stability of a system. Extending this concept to multidimensional abstract spaces, such a condition would offer the additional advantage of not having to explore derivatives in all different directions, when those are hard to compute.

In this Letter, we show that this is indeed possible by calculating eigenvalues of two-particle vertex functions. Even though a direct connection with the thermodynamic potentials is not obvious at first sight, here we demonstrate that the conditions based on the Hessian can be rewritten solely in terms of the single-particle propagator G and the eigenspectrum of the generalized two-particle susceptibility χ (see right-hand side of the sketch in Fig. 1). First, we derive the relevant thermodynamic stability criteria in terms of derivatives of the grand potential Ω for the single-band Hubbard model. Second, we make the connection to two-particle response functions χ, and show that the stability conditions can be rewritten in terms of their eigenvalues and eigenvectors, giving a clear-cut and compact criterion for the thermodynamic stability of a strongly correlated system. In doing so we also generalize our findings to

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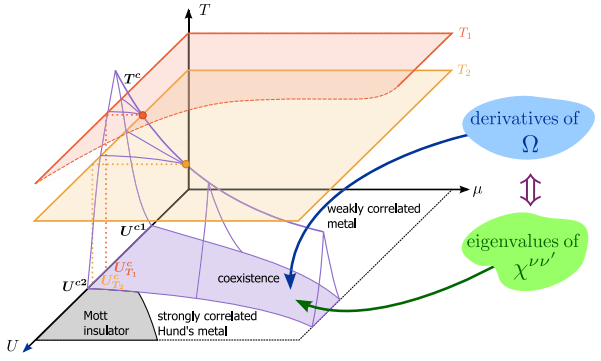

FIG. 1. Sketch of the phase diagram of the two-orbital Hubbard model described in Eq. (12) as a function of temperature T, interaction U, and chemical potential μ. The U axis is located at half filling and $T = 0$. At finite doping, the violet "moustache-shaped" region describes a coexistence regime of a weakly correlated and a strongly correlated (Hund's) metal.

generic two-body interactions as well as for the case of the presence of a magnetic field [7]. Eventually, we exemplify the validity of our criterion for a more general system, a multiorbital Hubbard model: we numerically explore the coexistence region in its phase diagram with chemical potential μ, temperature T, and interaction strength U, where the thermodynamic analysis is relevant to assess the stability of the various competing phases (see Fig. 1).

Thermodynamic stability criteria for the Hubbard model—We first focus on the single-band Hubbard model [15–20],

$$H = \sum_{ij\sigma} t_{ij} c^\dagger_{i\sigma} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} - \mu \sum_{i\sigma} n_{i\sigma}, \tag{1}$$

where t_{ij} are hopping amplitudes, $c^{(\dagger)}_{i\sigma}$ annihilates (creates) an electron with spin σ on site i, $n_{i\sigma}$ is the number operator, U the purely local Coulomb interaction, and μ the chemical potential. For this model, the grand potential (Landau free energy) $\Omega = -T \ln Z$ (with the partition function Z) is a function of the free parameters (T, μ, U) and its exact differential reads [21,22]

$$\frac{1}{V} d\Omega = -s dT - n d\mu + D dU, \tag{2}$$

where $(1/V)(\partial\Omega/\partial U) = D = \langle n_\uparrow n_\downarrow \rangle$ is the double occupancy, $-(1/V)(\partial\Omega/\partial\mu) = n$ the density, and $-(1/V)(\partial\Omega/\partial T) = s$ the entropy per lattice site at fixed volume V. The stability of the solutions requires its Hessian to be negative: $d^2\Omega < 0$ [7,21,23–26]. If we fix the temperature T, this explicitly means that

$$d^2\Omega = \begin{pmatrix} d\mu & dU \end{pmatrix} \begin{pmatrix} \frac{\partial^2\Omega}{\partial\mu^2} & \frac{\partial^2\Omega}{\partial U\partial\mu} \\ \frac{\partial^2\Omega}{\partial U\partial\mu} & \frac{\partial^2\Omega}{\partial U^2} \end{pmatrix} \begin{pmatrix} d\mu \\ dU \end{pmatrix} < 0. \tag{3}$$

The Hessian is negative definite (and, hence, the system is stable) if its principle minors are alternating in sign, beginning with a negative sign. This leads to the following general stability criteria:

$$\frac{\partial^2\Omega}{\partial\mu^2} < 0, \tag{4}$$

$$\frac{\partial^2\Omega}{\partial\mu^2}\frac{\partial^2\Omega}{\partial U^2} - \left[\frac{\partial^2\Omega}{\partial U\partial\mu}\right]^2 > 0. \tag{5}$$

Reexpressed in thermodynamic observables and parameters, these conditions read:

$$\frac{\partial n}{\partial\mu} > 0, \tag{6}$$

$$-\frac{\partial n}{\partial\mu}\frac{\partial D}{\partial U} - \left[\frac{\partial n}{\partial U}\right]^2 > 0 \tag{7}$$

$(-(\partial n/\partial U) = (\partial D/\partial\mu)$ holds as a Maxwell relation). Note that the first condition Eq. (6) is equivalent to the well-known criterion that in a thermodynamically stable system, the electronic compressibility has to be positive; i.e., $\kappa = (2/n^2)(\partial n/\partial\mu) > 0$. However, Eq. (6) is not a sufficient criterion, so that for a system to be thermodynamically stable, also Eq. (7) has to hold [27].

Connection to two-particle response functions—After deriving the above stability criteria, let us now relate them to the structure of two-particle response functions. In particular, the momentum-dependent static charge susceptibility of the system is given by $\chi(\mathbf{q}) = \frac{1}{2}\int_0^\beta d\tau \langle n(\mathbf{q},\tau) n(-\mathbf{q},0)\rangle - \langle n\rangle^2$, where $\beta = 1/(k_B T)$ and $n(\mathbf{q}) = (1/V)\sum_{\mathbf{k}\sigma} c^\dagger_{\mathbf{k}+\mathbf{q}\sigma} c_{\mathbf{k}\sigma}$. Then the corresponding local susceptibility $\chi_{\rm loc}$ can be obtained by summing over all momenta $\mathbf{q}$.

The latter response function can be either directly measured by applying a local external field coupled to the charge degrees of freedom or obtained by summing the so-called (local) generalized susceptibility $\chi^{\nu\nu'}$ [7,29–34] at zero bosonic transfer frequency $\Omega = 0$ over the two fermionic Matsubara frequencies ν and ν':

$$\chi_{\rm loc} = \frac{1}{\beta^2}\sum_{\nu\nu'} \chi^{\nu\nu'}(\Omega = 0) = \sum_\alpha \lambda_\alpha w_\alpha. \tag{8}$$

The last equality represents the decomposition in the eigenbasis of $\chi^{\nu\nu'}(\Omega = 0)$ with eigenvalues λ_α and eigenvectors V_α constituting the respective spectral weights $w_\alpha = [(1/\beta)\sum_\nu V_\alpha^{-1}(\nu)][(1/\beta)\sum_{\nu'} V_\alpha(\nu')]$ [30,35]. The connection between the local susceptibility and the electronic compressibility becomes particularly transparent within the dynamical mean-field theory (DMFT) [36–40], which is the exact solution of Eq. (1) in the limit of infinite lattice connectivity. In the case of the Bethe lattice nonlocal correlation functions can be analytically expressed [30,36,41,42] in terms of purely local functions

[31,33,43,44]. In particular, the following expression for the compressibility $\kappa = (2/n^2)\chi(\mathbf{q}=0)$ holds:

$$\kappa = \frac{2}{n^2\beta^2}\sum_{\nu\nu'}\left[\chi^{-1}_{\nu\nu'} + \frac{t^2}{\beta}\delta_{\nu\nu'}\right]^{-1} = \frac{2}{n^2}\sum_{\alpha}\left[\frac{1}{\lambda_\alpha}+\frac{t^2}{\beta}\right]^{-1} w_\alpha. \tag{9}$$

Here one can immediately recognize that the first stability criterion, Eq. (6), namely that κ should be positive, is intimately related to the spectrum of the generalized local charge susceptibility. This is quite remarkable, since κ is a lattice quantity, whereas $\chi^{\nu\nu'}$ represents a purely local impurity quantity. Actually, as we derive in detail in [7], *both* stability criteria Eqs. (6) and (7) depend directly on the eigenvalues λ_α and (via accompanying weights w_α, v_α, y_α) on the eigenvectors V_α of $\chi^{\nu\nu'}$:

$$\kappa = \frac{2}{n^2}\sum_{\alpha}\left[\frac{1}{\lambda_\alpha}+\frac{t^2}{\beta}\right]^{-1} w_\alpha > 0, \tag{10}$$

$$-n^2\kappa\left[-\frac{D}{U}+\sum_\alpha \frac{1}{\frac{1}{\lambda_\alpha}+\frac{t^2}{\beta}}v_\alpha\right] - \left[\sum_\alpha \frac{2}{\frac{1}{\lambda_\alpha}+\frac{t^2}{\beta}}y_\alpha\right] > 0, \tag{11}$$

where $y_\alpha = \left[(1/\beta)\sum_\nu V_\alpha(\nu)\right]\left[-(1/\beta)\sum_\nu V_\alpha^{-1}(\nu)(\partial\Sigma/\partial U)\big|_G\right]$ and $v_\alpha = \left[(1/\beta)\sum_\nu V_\alpha(\nu)(\tilde{\chi}_0^\nu/\chi_0^\nu)\right]\left[-(1/\beta)\sum_\nu V_\alpha^{-1}(\nu)(\partial\Sigma/\partial U)\big|_G\right]$, with $(\partial\Sigma/\partial U)\big|_G = (1/2U)\left[(1/\beta)\sum_{\nu'}\Gamma_d^{\nu\nu'}G_{\nu'}+\Sigma_\nu\right]$ being the explicit derivative of the self-energy with respect to the interaction fixing the Green's function, the lattice bubble $\chi_0^\nu(\mathbf{q}=0) = -(\beta/V)\sum_{\mathbf{k}} G_k^2$, and the expression $\tilde{\chi}_0^\nu(\mathbf{q}=0) = -(\beta/VU)\sum_{\mathbf{k}} G_k^2[i\nu+\mu-\epsilon_{\mathbf{k}}]$.

Thus, we have expressed all thermodynamic derivatives given in Eqs. (6) and (7) by single- and two-particle correlation functions evaluated for a given parameter set. This result, which applies even to the exact solution of the Hubbard model at finite lattice connectivity, is particularly remarkable since one would have naively expected that their determination had also required the knowledge of higher order correlation functions [7]. This way we managed to translate conditions on thermodynamic derivatives into conditions on the eigenspectrum of χ. In particular, if the value of the lowest eigenvalue λ_1 falls below the lower bound $-\beta/t^2$ [45], κ in Eq. (10) turns negative, hence signaling an instability of the system. Violations of the second condition Eq. (11) are also dictated by the eigenvalues and eigenvectors of χ. It is important to note that such a connection between derivatives of thermodynamic potentials and the eigenspectrum of the generalized susceptibility can be readily extended to the case with more than one orbital, as well as to general two-body interactions, finite dimensions, and the case of the presence of a magnetic field [7].

Stability analysis close to a Mott transition—To show the validity of our reformulated thermodynamic analysis, we investigate a many-body Hamiltonian which possesses an extended region of instability in the proximity to a Mott transition. In general, the parameter ranges where such an instability occurs are larger in multiorbital than single-band models [49]. For this reason, we address a two-orbital Hubbard model (see, e.g., [6,50]) and consider again the Bethe lattice. We use DMFT to study the paramagnetic phase and consider an interaction of density-density Hubbard form:

$$\begin{aligned} H = &\sum_{\langle i,j\rangle,m,\sigma} t_{ij}c^\dagger_{im\sigma}c_{jm\sigma} + U\sum_{im} n_{im\uparrow}n_{im\downarrow} \\ &+ (U-2J)\sum_{im,m'\neq m} n_{im\uparrow}n_{im'\downarrow} \\ &+ (U-3J)\sum_{i,m<m',\sigma} n_{im\sigma}n_{im'\sigma} - \mu\sum_{im\sigma} n_{im\sigma}, \end{aligned} \tag{12}$$

with $c^{(\dagger)}_{im\sigma}$ annihilating (creating) an electron on lattice site i in orbital $m\in\{1,2\}$ and with spin σ, density operators $n_{im\sigma} = c^\dagger_{im\sigma}c_{im\sigma}$, nearest-neighbor hopping matrix elements t_{ij}, and as interaction parameters the on-site same-orbital repulsion U and Hund's exchange coupling J which we fix to $J = U/4$.

As sketched in the phase diagram as a function of (T,μ,U) of Fig. 1, the system undergoes a first-order transition from a (weakly) correlated metal to a Mott insulator at U^{c2} at $T=0$ and half filling, upon increasing U [6]. Starting from the opposite strong coupling limit, the metallic solution sets in only at $U^{c1} < U^{c2}$ and, hence, a hysteresis region appears for $U^{c1} < U < U^{c2}$. In this region, the equation of state of the system is multivalued and the insulating coexists with the metallic solution. At finite doping both solutions become metallic; however, they evolve differently when changing the chemical potential μ: the former Mott insulator turns into a strongly correlated Hund's metal [51], separated from the weakly correlated metal by a coexistence zone (violet-shaded "moustache" shape). This coexistence regime shows phase separation and is therefore thermodynamically unstable. At finite temperatures, the phase-separation region shrinks, terminating at a line of second-order critical end points (T^c,μ^c,U^c).

After these general considerations, let us now illustrate our results, focusing on two specific temperatures: $T_1 = 1/35$ (Fig. 2) and $T_2 = 1/50$ (Fig. 3). The overall behavior at different temperatures looks quite similar. However, we will show that for the dataset we consider at the lowest temperature T_2 the system becomes thermodynamically unstable by violating the stability criteria in a qualitatively different way than for the dataset at T_1. We start with the higher value T_1. In Fig. 2(a) we show the total electron filling $n = \sum_{im\sigma}\langle n_{im\sigma}\rangle$ as a function of the chemical

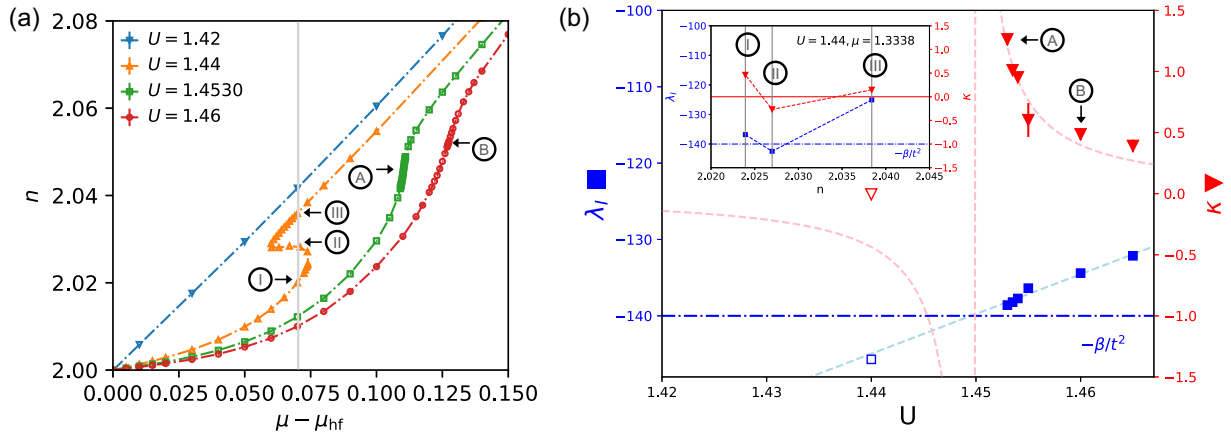

FIG. 2. DMFT calculations of the two-orbital Hubbard model on the Bethe lattice at $T_1 = 1/35$. (a) n versus $\mu - \mu_{\mathrm{hf}}$ for several values of the interaction U. A and B indicate the respective maxima in κ for two different interaction values. The vertical gray line indicates the cut at constant chemical potential $\mu = 1.3338$ corresponding to the inset in (b), I–III indicate the respective points for $U = 1.44$. (b) Lowest eigenvalue λ_I of the generalized static local charge susceptibility $\chi^{\nu\nu'}$ (blue squares) and the corresponding values of the charge susceptibility κ (red triangles). Here, the values of the respective maxima of κ are shown. The dashed gray lines are fits of the values of κ [Eq. (9)] and λ_I (linear), respectively, and serve as guide to the eye. Inset: cut at constant interaction $U = 1.44$ and chemical potential [corresponding to the solid gray line in (a)].

potential (measured from the chemical potential at half filling) for several values of U. On the metallic branch the filling depends approximately linearly on the chemical potential, which is the case for the line of $U = 1.42$ [52]. Here, the electronic compressibility $\kappa = 1/n^2 \partial n/\partial \mu$ assumes moderate values ($\kappa \approx 0.15$).

Approaching the region of phase separation from larger interaction values, we observe a dramatic sharpening of this crossover: at $U = 1.46$ we clearly see the onset of a stretched S-shaped curve, which assumes its maximum value of $\kappa \approx 0.5$ at point B in Fig. 2(a). A small decrease of the interaction to $U = 1.453$ results in an even larger compressibility of $\kappa \approx 1.25$ before it eventually diverges, giving rise to the "distorted" S-shaped curve of $U = 1.44$. Tracing the (n, μ) curve at this particular value of the interaction reveals three distinct regimes [of which we mark three representative points in Fig. 2(a)]: a strongly correlated metallic regime I and a weakly correlated metallic regime III, connected by an unstable solution II. At the boundaries of the stable branches, the compressibility diverges. The (discontinuous) jump from one stable solution to the other would correspond to a Maxwell construction [6].

We now more closely inspect the electronic compressibility and its connection to the eigenvalue structure of $\chi^{\nu\nu'}$. Figure 2(b) shows the maximum values of κ (red triangles) as well as the value of the smallest (leading) eigenvalue of $\chi^{\nu\nu'}$, λ_I (blue squares), for several values of the interaction. With λ_I we can understand the increase of κ when decreasing U, since the leading eigenvalue becomes more negative. Eventually, λ_I approaches $-\beta/t^2 = -140$, at which value Eq. (6) indicates that $\kappa \to \infty$ [30]. Immediately after the divergence, κ assumes a negative value, thus violating the first stability condition Eq. (6). To emphasize this violation, in the inset of Fig. 2(b) we show λ_I and κ as a function of the total filling for the points I–III at fixed $U = 1.44$ and $\mu = 1.3338$ [corresponding to the gray vertical line in Fig. 2(a)]. One can see that, in this case, for the two stable branches, $\kappa > 0$ and $\lambda_I > -\beta/t^2$, whereas for the unstable branch, $\kappa < 0$ and $\lambda_I \approx -142 < -\beta/t^2$.

Calculations at the lower temperature $T_2 = 1/50$ demonstrate that the system can become thermodynamically unstable even if the compressibility is positive. This is shown in Fig. 3. In Fig. 3(a) we can see that the overall behavior of $\langle n \rangle$ as a function of μ is very similar to the behavior at elevated temperatures (linear behavior away from the coexistence region, S shape coming close to it). Additionally, branches connecting the two different metallic regimes are again appearing. In the case of $U = 1.46$ we can see that this *clearly unstable* branch contains a regime (e.g., point II) with *positive* compressibility. Repeating our analysis of the leading eigenvalues λ_I in Fig. 3(b), we see that, also for T_2, when λ_I is approaching the limit $-\beta/t^2 = -200$, the compressibility diverges $\kappa \to \infty$. The inset again shows that, for $U = 1.46$, the leading eigenvalue is $\lambda_I \approx -216 < -\beta/t^2$ for the point on the unstable branch II. However, since the eigenvalue is farther away from the respective limit than in the case of T_1 in Fig. 2, κ remains positive.

Single criterion for thermodynamic (in)stability—The above numerical findings indeed demonstrate the significance of the eigenvalues of the generalized charge susceptibility for the thermodynamic stability of a strongly correlated system: if one of the eigenvalues falls below the limit $-\beta/t^2$, the relations Eqs. (6) and (7) are not fulfilled at the same time, rendering the system

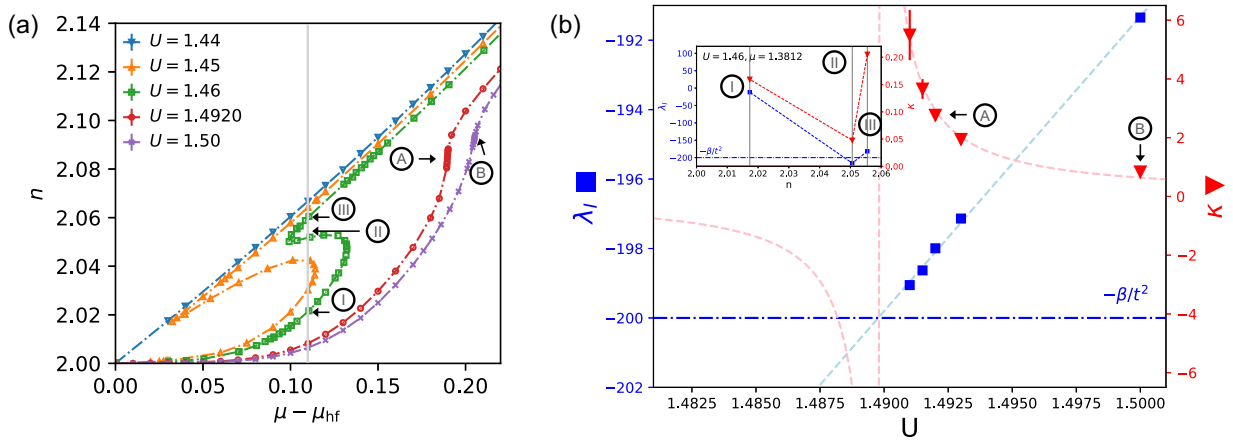

FIG. 3. Analogous plot to Fig. 2 for $T_2 = 1/50$.

thermodynamically unstable. The main player here can be identified with the lowest eigenvalue λ_I [7]. Inspecting the structure of the condition based on the eigenspectrum of χ more closely, one could argue that Eq. (7) is always violated close enough to the Mott metal-insulator transition at half filling. Indeed, $\kappa \propto \partial n/\partial\mu$ is strongly suppressed there and the first term in Eq. (7) could potentially become smaller than the second one. However, analyzing Eq. (11) tells us that in this situation both terms of the equation vanish with the same power law, and our numerical calculations show that the first term remains larger. The expression of the thermodynamic derivatives in terms of eigenvalues and eigenweights also explains why neither $(\partial n/\partial\mu)$ nor $(\partial n/\partial U)$ diverge at the critical end point at half filling, at odds with $(\partial D/\partial U)$ [4,26,30]. Thereby, we have also demonstrated a direct connection between $\lambda_I \to -\beta/t^2$ and $\partial D/\partial U \to \infty$ at the critical end point at half filling [2].

Conclusions—We have derived stability conditions for correlated fermionic matter at the one- and two-particle diagrammatic level by relating the conventional criteria involving derivatives of the grand potential to the eigenvalue structure of the generalized susceptibility [29,35,44]. We illustrated the applicability of our reformulation with the example of the coexistence region emerging in the proximity of the Hund's Mott metal-insulator transition in a two-band Hubbard model. There, in addition to the unstable solution with negative compressibility, we were able to identify an unstable branch with *positive* compressibility. In this context we demonstrated that the eigenspectrum of the generalized susceptibility represents a clear-cut indicator for thermodynamic stability, conceptually changing the conventional viewpoint based on the evaluation of thermodynamic derivatives.

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[53] www.gauss-centre.eu.
[54] www.lrz.de.