Optical Sum Rules that Relate to the Potential Energy of Strongly Correlated Systems

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A class of sum rules for inelastic light scattering is developed. We show that the first moment of the nonresonant response provides information about the potential energy in strongly correlated systems. The polarization dependence of the sum rules provides information about the electronic excitations in different regions of the Brillouin zone. We determine the sum rule for the Falicov-Kimball model, which possesses a metal-insulator transition, and compare our results to the light scattering experiments in SmB_6.

One of the key signatures of strong electron correlations in condensed matter systems is the redistribution of spectral weight from low to high energies. A classic example of this phenomenon occurs when a normal metal becomes a superconductor at low temperatures. The optical conductivity is suppressed at low energy due to the presence of the superconducting gap [1]. Because there is an optical sum rule—the f-sum rule—which constrains the integrated spectral weight in $\sigma(\nu)$, the spectral weight suppressed below the superconducting energy gap reappears as a delta function peak at $\nu = 0$, reflecting the onset of many-body coherence in the system. In high temperature superconductors, low-energy spectral weight has also been observed to shift to high energies below the superconducting transition [2]. This dramatic spectral weight transfer is believed to be a signature of the strong electronic correlations in these and related materials [3].

The use of sum rules in optical conductivity measurements has had a wide impact in a number of fields of science. The optical sum rule originated in atomic physics as a relationship between the total number of electrons in the atomic system and the integrated spectral weight [4]. In a solid state system, the optical sum rule is usually projected onto the lowest energy band. In this case, the integrated spectral weight associated with electrons in the lowest band is related to the average kinetic energy of the electrons, regardless of the nature of the electronic interactions [5]. Since the electronic kinetic energy usually varies on an energy scale on the order of electron volts, the average kinetic energy is essentially a constant at low to moderate temperatures, and so the optical conductivity sum rule is essentially temperature independent.

It would be useful to have similar sum rules that relate to the potential energy. In strongly correlated electron systems in which electronic interaction energies are on the order of, or greater than, the kinetic energy, efforts to study the potential energy as functions of doping, pressure, or temperature have been hindered by the limited tools available for measuring dynamical properties. We show here that the nonresonant inelastic light scattering response has

sum rules similar to the f-sum rule that relate to the potential energy, and that these sum rules should provide valuable insight into the scattering of optical or x-ray photons from materials [6]. As an added benefit compared to optical conductivity measurements, inelastic light scattering allows one to probe the electronic excitations in different regions of the Brillouin zone (BZ) by orienting the incident and scattered light polarizations. Our approach shares some similarities with work performed on higher-moment sum rules of the optical conductivity in a model with an Umklapp scattering potential [7].

Shastry and Shraiman [8] were the first to point out that, if the self-energy is local and $d \to \infty$, the optical conductivity and the nonresonant Raman response function in the depolarized (incident photon polarization ϵ_I perpendicular to the scattered photon polarization ϵ_S) scattering geometry are related according to $\sigma(\nu) \propto S(\nu)/\nu$, a relationship that was proved in Ref. [9]. This result implies that there is also a sum rule for Raman scattering, which is related to the f-sum rule for the optical conductivity and to the average kinetic-energy of the electrons.

In this Letter, we show that there are also interaction-dependent sum rules for inelastic light scattering that are related to the potential energy for $\mathbf{q} = 0$ Raman scattering, and to combinations of the potential and kinetic energies for $\mathbf{q} \neq 0$ inelastic x-ray scattering.

The formalism used to derive these sum rules is straightforward. If we consider the time-ordered product that yields the susceptibility corresponding to the fluctuations of an operator $\mathcal{O}$

$$\chi(\tau) = \text{Tr}\langle \mathcal{T}_\tau e^{-\beta\mathcal{H}} \mathcal{O}(\tau)\mathcal{O}^\dagger(0)\rangle/Z - (\text{Tr}\langle e^{-\beta\mathcal{H}}\mathcal{O}\rangle/Z)^2,$$

$$(1)$$

where τ is the imaginary time, $\mathcal{H}$ is the Hamiltonian, β is the inverse temperature, $Z = \text{Tr}e^{-\beta\mathcal{H}}$ is the partition function, and $\mathcal{O}(\tau) = e^{\tau\mathcal{H}}\mathcal{O}e^{-\tau\mathcal{H}}$. Then it is easy to show from the Lehmann representation that when the susceptibility is Fourier transformed, and analytically continued to the real frequency axis, we get

$$\int_0^\infty d\nu \, \nu \, \mathrm{Im}\chi(q,\nu) = \frac{\pi}{2}\mathrm{Tr}\langle e^{-\beta\mathcal{H}}[\mathcal{O},[\mathcal{H},\mathcal{O}^\dagger]]\rangle/Z \quad (2)$$

as the general sum rule for the first moment of the susceptibility (the brackets indicate commutators). If we consider the polarization operator $\mathcal{O}_{\mathrm{pol}} = e\Sigma_i \mathbf{R_i}n_i$ with n_i the number density operator at site i, then this gives the f-sum rule where $\sigma(\nu) = \mathrm{Im}\chi_{JJ}(\nu)/\hbar\nu$ in terms of the current-current correlation function χ_{JJ} (with $J = i[\mathcal{H},\mathcal{O}_{\mathrm{pol}}]/\hbar$):

$$\int_0^\infty d\nu\,\sigma(\nu) = \frac{\pi e^2 a^2}{2\hbar}\mathrm{Tr}\langle e^{-\beta\mathcal{H}}(-\hat{T})\rangle/Z, \quad (3)$$

with a the lattice spacing. The sum rule is proportional to the average kinetic energy (we consider only nearest-neighbor hopping on a hypercubic lattice $\hat{T} = -t\Sigma_{i,\delta,\sigma}c_{i,\sigma}^\dagger c_{i+\delta,\sigma}$ with δ a nearest-neighbor translation vector). Likewise, if we consider the dynamical charge susceptibility $\mathcal{O}_{\mathrm{ch}}(\mathbf{q}) = \Sigma_k c_{\mathbf{k}+\mathbf{q}/2,\sigma}^\dagger c_{\mathbf{k}-\mathbf{q}/2,\sigma}$ we obtain

$$\int_0^\infty d\nu\,\nu\,\mathrm{Im}\chi_{\mathrm{ch}}(\mathbf{q},\nu) = \frac{\pi}{2}\mathrm{Tr}\Big\langle e^{-\beta H}\sum_{\mathbf{k}}[\epsilon(\mathbf{k}+\mathbf{q})+\epsilon(\mathbf{k}-\mathbf{q})-2\epsilon(\mathbf{k})]\Big\rangle\Big/Z = \pi(1-X)\mathrm{Tr}\langle e^{-\beta\mathcal{H}}(-\hat{T})\rangle/Z \quad (\text{in } d\to\infty) \quad (4)$$

with $X = \lim_{d\to\infty}\Sigma_{i=1}^d \cos(k_i)/d$ and $\epsilon(\mathbf{q})$ the band structure. This vanishes as q^2 for $\mathbf{q}=0$ as it must, due to total charge conservation.

There is, however, no charge conservation for inelastic light scattering with $\mathbf{q}=0$ optical photons (Raman scattering). Raman scattering can be classified into representations of the irreducible point group symmetry of the crystal, selected by orienting the incident and scattered polarization vectors. The light scattering polarizations allow energy fluctuations to be projected onto different regions of the BZ, which has been useful in elucidating the behavior of electron dynamics for different momentum states [10]. For example, for nonresonant scattering in tetragonal systems, the operator $\mathcal{O}_{A_{1g}}(\mathbf{q}) = \Sigma_{\mathbf{k}}\epsilon(\mathbf{k})c_{\mathbf{k}+\mathbf{q}/2}^\dagger \times c_{\mathbf{k}-\mathbf{q}/2} = \hat{T}(\mathbf{q})$ is the kinetic-energy operator for A_{1g} scattering, and $\mathcal{O}_{B_{1g}}(\mathbf{q}) = \Sigma_{\mathbf{k}}\epsilon(\mathbf{k}+\mathbf{Q})c_{\mathbf{k}+\mathbf{q}/2}^\dagger c_{\mathbf{k}-\mathbf{q}/2}$ is a modified kinetic-energy operator for B_{1g} scattering for the zone boundary wave vector $\mathbf{Q} = (\pi,0)$ [which is generalized to higher dimensions as $\mathbf{Q} = (\pi,0,\pi,0,\ldots)$]. Thus the A_{1g} scattering response is associated with energy fluctuations from all regions of the BZ, while the B_{1g} response is associated with dynamics near the BZ edges and away from the diagonals. The sum rule in Eq. (2) for nonresonant light scattering is similar to the optical sum rule, except the (model-dependent) operator average is different, and now depends on the potential energy since $\mathcal{H} = \hat{T} + \hat{V}$ [see Eq. (2)]. In the general case, there are two contributions: one from the kinetic-energy commutator and one from the potential energy commutator:

$$\int_0^\infty d\nu\,\nu\,\mathrm{Im}\chi_{\mathrm{in}}(\mathbf{q},\nu) = \frac{\pi}{2Z}\mathrm{Tr}\langle e^{-\beta\mathcal{H}}[\hat{T}(\mathbf{q},\mathbf{Q})+\hat{U}(\mathbf{q},\mathbf{Q})]\rangle. \quad (5)$$

The first term on the right-hand side of Eq. (5) does not depend on the type of Hamiltonian and is given by $\hat{T}(\mathbf{q},\mathbf{Q}) = -\Sigma_{\mathbf{k},\sigma}t(\mathbf{k},\mathbf{q},\mathbf{Q})c_{\mathbf{k},\sigma}^\dagger c_{\mathbf{k},\sigma}$, with $t(\mathbf{k},\mathbf{q},\mathbf{Q}) = \epsilon(\mathbf{k}-\mathbf{Q}-\mathbf{q}/2)^2[\epsilon(\mathbf{k}-\mathbf{q})-\epsilon(\mathbf{k})] + \epsilon(\mathbf{k}-\mathbf{Q}+\mathbf{q}/2)^2 \times [\epsilon(\mathbf{k}+\mathbf{q})-\epsilon(\mathbf{k})]$. Regardless of the symmetry [$\mathbf{Q}=0$ for A_{1g} or $(\pi,0)$ for B_{1g}] the kinetic-energy part of the sum rule does not contribute to the ($\mathbf{q}=0$) Raman scatter-

ing response, but it does contribute to the ($\mathbf{q}\neq0$) inelastic x-ray scattering response in a polarization-dependent manner.

However the second term in Eq. (5) depends on the particular choice for the potential energy in the Hamiltonian. Evaluating these sum rules for different models is complicated, because the operator averages involve complex correlation functions. We consider the simplest model here, the spinless Falicov-Kimball model (FK) [11]

$$\mathcal{H}_{\mathrm{FK}} = -\frac{t^*}{2\sqrt{d}}\sum_{\langle i,j\rangle}c_i^\dagger c_j + U\sum_i c_i^\dagger c_i w_i. \quad (6)$$

Here $c_i^\dagger (c_i)$ creates (destroys) a conduction electron at site i, w_i is a classical variable (representing the localized electron number at site i) that equals 0 or 1, t^* is a renormalized hopping matrix that is nonzero between nearest neighbors on a hypercubic lattice in d dimensions [12], U is the local screened Coulomb interaction between conduction and localized electrons, and $\langle i,j\rangle$ denotes a sum over sites i and nearest neighbors j. We set the average filling for conduction and localized electrons to $1/2$.

For the FK model, the operator $\hat{U}$ in the sum rule is

$$\hat{U}_{\mathrm{FK}}(\mathbf{q},\mathbf{Q}) = \frac{Ut^{*2}}{2dN}\sum_{\mathbf{i},\delta,\delta'}c_i^\dagger c_{i+\delta+\delta'}e^{-i\mathbf{Q}\cdot(\delta+\delta')}$$
$$\times [e^{-iq/2\cdot(\delta+\delta')}(w_{\mathbf{i}+\delta'} - w_{\mathbf{i}+\delta+\delta'})$$
$$- e^{iq/2\cdot(\delta+\delta')}(w_{\mathbf{i}} - w_{\mathbf{i}+\delta})]. \quad (7)$$

This operator involves the difference of correlated hopping operators, where the hopping of the conduction electrons is correlated with the presence of the localized electrons; note how the potential energy directly enters when $\delta + \delta' = 0$. The operator for the Hubbard model is similar, but involves complex spin and spin-flip hopping correlation functions.

The result in Eq. (8) is valid for any dimension. It can be evaluated exactly by examining the large dimensional limit using results from dynamical mean field theory (DMFT) [13]. The result for the FK model is

$$\int_0^\infty d\nu\,\nu\,\mathrm{Im}\chi_{\mathrm{in}}(\mathbf{q},\nu)=\frac{\pi}{2Z}\mathrm{Tr}\langle\hat{T}(\mathbf{q},\mathbf{Q})+\hat{U}(\mathbf{q},\mathbf{Q})\rangle$$

$$=\mathrm{Im}\int d\omega f(\omega)\left\{(1-X)X'^2\left[1-\frac{3}{2}Z(\omega)G(\omega)-Z^2(\omega)[1-Z(\omega)G(\omega)]\right]+\frac{1}{2}(X-1)[1-Z(\omega)G(\omega)]\right\}$$

$$+\mathrm{Im}\int d\omega f(\omega)(\Sigma(\omega)-U\langle w_i\rangle)\left\{\frac{1-X'^2}{2}G(\omega)+\{Z(\omega)-1/G(\omega)\}X'^2\right\},\qquad(8)$$

with $f(\omega)=1/[1+\exp(\beta\omega)]$ the Fermi function, $G(\omega)$ and $\Sigma(\omega)$ the Green's function and self-energy, respectively, and $Z(\omega)=\omega+\mu-\Sigma(\omega)$. The difference between A_{1g} and B_{1g} scattering comes from the momentum factors $X'=\lim_{d\to\infty}(1/d)\Sigma_{i=1}^d\cos(q_i/2)h^i$, with $h=1(-1)$ for $A_{1g}(B_{1g})$ scattering. Note that both the first term associated with the kinetic energy and the second term associated with the potential energy contribute to the sum rule for inelastic x-ray scattering ($\mathbf{q}\neq0$). On the other hand, only the second "potential energy" term contributes to the sum rule for Raman scattering ($\mathbf{q}=0$). Therefore, the sum rule's momentum dependence contains information regarding the potential and kinetic-energy contributions.

Note that the sum rule for ($X=1$) Raman scattering is proportional to the correlated part of the self-energy, due to the factor $\Sigma(\omega)-U\langle w_i\rangle$ which has the Hartree shift subtracted off. Further, we note that in DMFT, where the self-energy is local (and $d\to\infty$), the sum rule for B_{1g} Raman scattering would also apply to the second moment of the optical conductivity:

$$\int_0^\infty d\nu\,\nu\,\mathrm{Im}\chi_{B_{1g}}(\mathbf{q}=0,\nu)\propto\int_0^\infty d\nu\,\nu^2\sigma(\nu).\qquad(9)$$

However, this relationship is violated in finite dimensions whether or not the self-energy has momentum dependence.

We plot the sum rule for the FK model in Fig. 1 for B_{1g} Raman scattering ($\mathbf{q}=0$) and different values of U as a function of temperature (results for A_{1g} are similar). We have verified that an explicit integral of the nonresonant

Raman response agrees with the sum rule plotted in Fig. 1 for many different values of U and T. We expect similar results to hold for other models of correlated electrons like the Hubbard model. Figure 1 shows that these sum rules are essentially constant at low temperature, indicating (i) the sum rule can be used to calibrate data from different samples and different temperatures; (ii) the sum rule can be used to determine the frequency above which interband transitions become prominent; (iii) the Raman response function multiplied by the frequency should be used to track spectral weight shifts because of the sum rule; and (iv) the sum rules have a momentum dependence for inelastic x-ray scattering that can be calculated and compared to experiment. Note that unlike the f-sum rule, which is evenly weighted throughout the spectral range, the Raman sum rules are heavily weighted at higher energies due to the multiplication by the frequency. Consequently, unless there is a clear separation between low and high energy bands in the system, higher energy bands can significantly distort the sum rule.

The momentum dependence of the sum rule is reduced as U increases and the physical properties become more local. The sum rule generally increases for increasing momentum transfer since the kinetic-energy term in Eq. (8) contributes to the sum rule as phase space is created for light scattering by increasing $\mathbf{q}$.

The underlying metal-insulator transition (MIT) is revealed via a simple scaling analysis, shown in Fig. 2. It can be shown that for metallic systems the sum rule varies as U^2 for small U, with large deviations occurring as the MIT
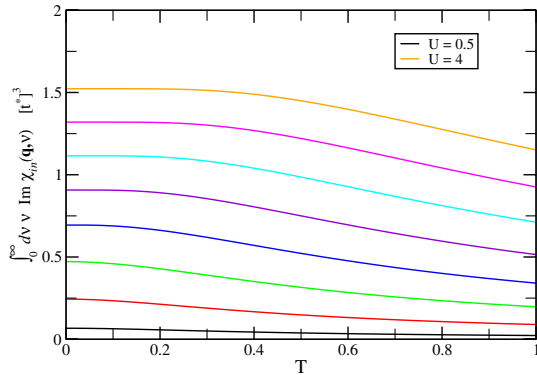

FIG. 1 (color online). B_{1g} sum rules as a function of temperature for the spinless FK model solved within DMFT (the A_{1g} results are similar). The different curves correspond to different values of the interaction strength increasing in steps of 0.5 from 0.5 on the lowest curve to 4.0 on the highest curve.
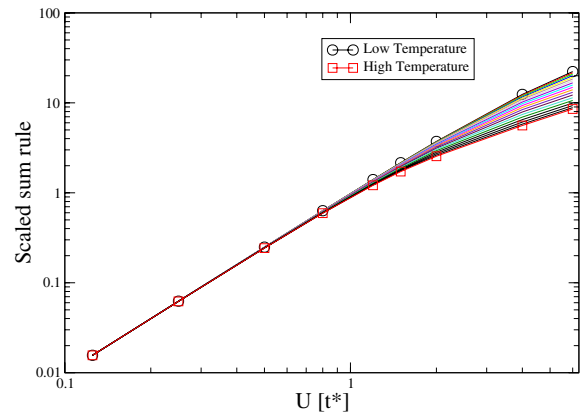

FIG. 2 (color online). B_{1g} scaled sum rules showing the scaling behavior with U^2 for the FK model discussed in the text. Deviations in scaling occur when $U\gtrsim U_c=\sqrt{2}t^*$, the critical value of U for the metal-insulator transition in the half-filled FK model.
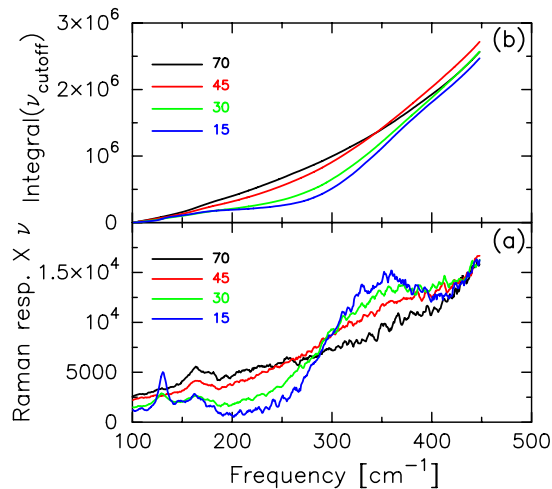
FIG. 3 (color online).   (a) Raman response multiplied by frequency for SmB_6 at four different temperatures (in K). (b) Corresponding plot of the integrated sum rule as a function of the frequency cutoff. All curves in (a) and (b) are plotted in arbitrary units.

is approached. In Fig. 2 we plot the sum rule divided by U^2 for different temperatures as a function of U. We see that the sum-rule data collapses for small U onto a single line for all temperatures. The scaled data abruptly fans out from the straight line at approximately $U = U_c$ and a strong temperature dependence emerges for larger U. Thus the onset of a strong temperature dependence and deviations from U^2 scaling can be used as a straightforward and quantitative way to identify a MIT from the optical data.

We show the relevance of these sum rules to an experimental system that is ideal for this situation, SmB_6. The Raman results on SmB_6 [14] provide an ideal comparison to this model for several reasons: the spectra have a clear separation between the low-energy (intraband) and high-energy (interband) scattering contributions; only the low-energy component in SmB_6 exhibits significant spectral weight changes due to the gap formation at low temperatures; and the photon energy used in the experiment lies in a gap in the density of states of SmB_6, and therefore the Raman response is not likely to be influenced by resonant or mixed-scattering effects. When we take the Raman data, and multiply by the frequency, we find that the sum rule holds to within 5% in this system (see Fig. 3), confirming the behavior determined from the FK model in DMFT (Fig. 1).

In summary, we have discovered sum rules for inelastic light scattering that are useful in analyzing both Raman scattering and inelastic x-ray scattering. The sum rules depend crucially on the form of the electron interactions, and thereby yield useful information about the correlations in the material. While light scattering data on correlated metals or insulators is still rather limited (particularly with regard to inelastic x-ray scattering), our sum rules may be employed to analyze data and elucidate how the kinetic and

potential energy of the system evolves as a function of doping, pressure, or temperature. The existence of a sum rule implies that it can be employed to calibrate light scattering data (especially for inelastic x-ray scattering) and it can be employed to try to discriminate between different strongly correlated models. We believe the two best methods for doing this are as follows: (i) compare the efficacy with which different models satisfy both the measured optical conductivity f-sum rule and the measured Raman scattering sum rules for different polarizations, or (ii) measure the temperature dependence of the Raman scattering sum rule for a range of temperatures, then compare this measurement with the calculated temperature dependence obtained using different models.

[1] P. L. Richards and M. Tinkham, Phys. Rev. Lett. **1**, 318 (1958).

[2] J. E. Hirsch, Physica (Amsterdam) **201C**, 347 (1992); D. N. Basov *et al.*, Science **283**, 49 (1999); J. E. Hirsch and F. Marsiglio, Phys. Rev. B **62**, 15131 (2000); J. E. Hirsch, Science **295**, 2226 (2002); H. J. A. Molegraaf *et al.*, Science **295**, 2239 (2002); A. B. Kuzmenko *et al.*, Phys. Rev. Lett. **91**, 037004 (2003).

[3] T. Osafune *et al.*, Phys. Rev. Lett. **82**, 1313 (1999).

[4] W. Thomas, Naturwissenschaften **13**, 627 (1925); W. Kuhn, Z. Phys. **33**, 408 (1925).

[5] P. F. Maldague, Phys. Rev. B **16**, 2437 (1977).

[6] We note that a symmetry dependent sum rule for *resonant* inelastic x-ray scattering in a single-ion model has been considered in M. van Veenendaal, P. Carra, and B. T. Thole, Phys. Rev. B **54**, 16010 (1996), and F. Borgatti *et al.*, Phys. Rev. B **69**, 134420 (2004). However these treatments can not be applied to systems near a metal-insulator transition nor to systems in which nonresonant scattering is important.

[7] M. Turlakov, J. Phys. A **36**, 9399 (2003); M. Turlakov and A. J. Leggett, Phys. Rev. B **67**, 094517 (2003).

[8] B. S. Shastry and B. I. Shraiman, Phys. Rev. Lett. **65**, 1068 (1990); Int. J. Mod. Phys. B **5**, 365 (1991).

[9] J. K. Freericks and T. P. Devereaux, Phys. Rev. B **64**, 125110 (2001).

[10] F. Venturini *et al.*, Phys. Rev. Lett. **89**, 107003 (2002).

[11] L. M. Falicov and J. C. Kimball, Phys. Rev. Lett. **22**, 997 (1969).

[12] W. Metzner and D. Vollhardt, Phys. Rev. Lett. **62**, 324 (1989).

[13] J. K. Freericks and V. Zlatić, Rev. Mod. Phys. **75**, 1333 (2003).

[14] P. Nyhus, S. L. Cooper, Z. Fisk, and J. Sarrao, Phys. Rev. B **52**, R14308 (1995); **55**, 12488 (1997).