Linear Response Calculations of Lattice Dynamics in Strongly Correlated Systems

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We introduce a new linear response method to study the lattice dynamics of materials with strong correlations. It is based on a combination of dynamical mean field theory of strongly correlated electrons and the local density functional theory of electronic structure. We apply the method to study the phonon dispersions of Mott insulators NiO and MnO in their paramagnetic insulating state not accessible by local density functionals. Our results are in good agreement with experiment.

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Computational studies of lattice dynamics and structural stability in strongly correlated electronic systems is a challenging theoretical problem. In the past density functional theory in its generalized gradient or local density approximations (LDA) [1] has delivered the full lattice dynamical information and electron-phonon related properties of a variety of simple metals and transition metals, as well as semiconductors with exceptional accuracy [2]. This is mainly due to the introduction of a linear response approach [3,4]. This method overcame the problems of traditional techniques based on static susceptibility calculations which generally fail to reproduce lattice dynamical properties of real materials due to difficulties connected with the summations in high-energy states and the inversion of very large dielectric matrix [5].

Despite these impressive successes, there is by now clear evidence that the present methodology fails when applied to strongly correlated materials. For example, the local density predictions for such properties as bulk modulus and elastic constants in metallic plutonium are approximately 1 order of magnitude off from experiment [6]; the phonon spectrum of Mott insulators such as MnO is not predicted correctly by LDA [7].

In this Letter we describe a new linear response method to study the lattice dynamics of correlated materials. It is based on the dynamical mean field theory (DMFT) [8], a many-body technique developed to study systems with strong on-site Coulomb repulsion. Recent progress in merging [9] this many-body description with the realistic LDA based electronic structure calculations has already led to new insights in long-standing problems, such as the temperature dependence of the magnetic properties of Fe and Ni [10], the volume collapse transition in Ce [11], and Pu [12,13]. We generalize this LDA + DMFT method to carry out linear response calculations by finding self-consistent changes in both charge densities and local Green functions induced by atomic displacements.

The LDA + DMFT approach computes the total energy, the charge density, and the local spectral function of the correlated electrons simultaneously. The latter spectra are known to be quite different for a strongly correlated system such as, e.g., heavy fermion metal, from the Kohn-Sham spectra of the local density functional theory due to the appearance of strongly renormalized quasiparticle features at the Fermi level and lower and upper Hubbard features or satellites at higher energies [8]. The LDA + DMFT technique can therefore provide a link between the photoemission spectra and the lattice dynamics of correlated materials, which is an interesting open problem.

As a test we consider two Mott-Hubbard systems NiO and MnO. Both materials are insulators with the energy gap of a few eV regardless whether they are antiferro- or paramagnetic. The spin dependent LSDA theory strongly underestimates the energy gap in the ordered phase and fails completely to describe the local moment regime reflecting a general drawback of band theory to have a wrong atomic limit. Therefore the real challenge for the theory is to describe the paramagnetic insulating state where the self-energy effects are crucial both for the electronic structure and for recovering the correct phonon dispersions in these materials. In this work we perform DMFT calculations by taking into account many-body effects among d electrons via self-consistent solution of the quantum impurity model [8]. The latter in the regime of large U adequate for both NiO and MnO in the paramagnetic phase can be treated within the well-known Hubbard 1 approximation. We show that our new method reproduces the properties of these materials in good agreement with the experiments. We discuss how correlations affect static dielectric properties and compare our results with the paramagnetic LDA and antiferromagnetic LSDA, LSDA + U solutions.

Our approach considers both the charge density ρ and the local Green function $\hat{G}(\omega)$ as parameters of a spectral density functional [13]. To find its extremum, a set of

Dyson equations is solved self-consistently:

$$[-\nabla^2 + V_{\text{eff}} + \hat{\Sigma}(\omega) - \hat{\Sigma}_{\text{dc}} - \epsilon_{\mathbf{k}j\omega}]\psi^r_{\mathbf{k}j\omega} = 0, \quad (1)$$

where V_{eff} is the effective potential of the local density functional and $\hat{\Sigma}(\omega)$ is the local self-energy operator. Since the local density approximation contains an average correlation energy, a double counting term $\hat{\Sigma}_{\text{dc}}$ appears in Eq. (1). Both V_{eff} and $\hat{\Sigma}(\omega)$ are functionals of the density and the local Green function which can be found using the formula

$$\hat{G}(\omega) = \sum_{\mathbf{k}j} \frac{\psi^l_{\mathbf{k}j\omega}\psi^r_{\mathbf{k}j\omega}}{\epsilon_{\mathbf{k}j\omega} - \omega}. \quad (2)$$

Note that the Green function is a non-Hermitian matrix that is frequency dependent so both the eigenvalues ϵ and right/left eigenvectors $\psi^{r,l}$ are treated formally as frequency dependent quantities: $\epsilon_{\mathbf{k}j\omega}$, $\psi^r_{\mathbf{k}j\omega}$, $\psi^l_{\mathbf{k}j\omega}$. (The latter satisfies the Dyson Eq. (1) with the wave function placed on the left.) In practice [9,12], Eq. (1) is solved on the Matsubara axis for a finite set of imaginary frequencies $i\omega_n$ using some localized orbital representation such as, e.g., linear muffin-tin orbitals (LMTOs) $\chi^{\mathbf{k}}_{\alpha}$ for the eigenvectors $\psi^r_{\mathbf{k}j\omega}$:

$$\psi^r_{\mathbf{k}j\omega} = \sum_{\alpha} A^{\mathbf{k}j\omega}_{\alpha}\chi^{\mathbf{k}}_{\alpha}, \quad (3)$$

which substitutes the differential Eq. (1) by a matrix eigenvalue problem.

Once the local Green function is constructed, the new charge density, the effective potential, and the local self-energy are computed. The latter is found by solving the Anderson impurity model using a suitable many-body technique. The entire formulation requires self-consistency which delivers the total energy of the interacting electronic system.

The dynamical matrix is the second order derivative of the energy. As with the ordinary density functional formulation of the problem [14], we deal with the first-order corrections to the charge density, $\delta\rho$, as well as the first-order correction to the local Green function $\delta\hat{G}(\omega)$ which should be considered as two independent variables in the functional of the dynamical matrix. To find the extremum, a set of the linearized Dyson equations has to be solved self-consistently:

$$\begin{aligned}[-\nabla^2 + V_{\text{eff}} + \hat{\Sigma}(\omega) - \hat{\Sigma}_{\text{dc}} - \epsilon_{\mathbf{k}j\omega}]\delta\psi^r_{\mathbf{k}j\omega} \\ + [\delta V_{\text{eff}} + \delta\hat{\Sigma}(\omega) - \delta\hat{\Sigma}_{\text{dc}}]\psi^r_{\mathbf{k}j\omega} = 0, \quad (4)\end{aligned}$$

which leads us to consider the first-order changes in the effective potential δV_{eff} and in the local self-energy operator $\delta\hat{\Sigma}(\omega)$. Here and in the following we will assume that the phonon wave vector of the perturbation $\mathbf{q}$ is different from zero, and, therefore, the first-order changes in the eigenvalues $\delta\epsilon_{\mathbf{k}j\omega}$ drop out. The quantities δV_{eff} and $\delta\hat{\Sigma}(\omega)$ are the functionals of $\delta\rho$ and $\delta\hat{G}(\omega)$ and should be found self-consistently. In particular, the change in the self-energy $\delta\hat{\Sigma}(\omega)$ assumes the development of solving an Anderson impurity model linearized with respect to atomic displacements.

In practice, change in the eigenvector $\delta\psi_{\mathbf{k}j\omega}$ has to be expanded in some basis set. Previous linear response schemes were based on tight-binding methods [15], plane wave pseudopotentials [3,4,16,17], linear augmented plane waves [18], mixed orbitals [19], and linear muffin-tin orbitals [20]. To build an effective computational scheme applicable for systems with localized orbitals we use LMTO representation as the basis. Because of its explicit dependence on the atomic positions, both Hellmann-Feynman contributions and incomplete basis set corrections appear in the expression for the dynamical matrix [14]. We expand $\delta\psi_{\mathbf{k}j\omega}$ as follows:

$$\delta\psi_{\mathbf{k}j\omega} = \sum_{\alpha}\{\delta A^{\mathbf{k}j\omega}_{\alpha}\chi^{\mathbf{k}+\mathbf{q}}_{\alpha} + A^{\mathbf{k}j\omega}_{\alpha}\delta\chi^{\mathbf{k}}_{\alpha}\}, \quad (5)$$

where we introduced both changes in the frequency dependent variational coefficients $\delta A^{\mathbf{k}j\omega}_{\alpha}$ as well as changes in the basis functions $\delta\chi^{\mathbf{k}}_{\alpha}$. The latter helps us to reach convergency in the entire expression (5) with respect to the number of the basis functions $\{\alpha\}$ fast since the contribution with $\delta\chi^{\mathbf{k}}_{\alpha}$ takes into account all rigid movements of the localized orbitals [20].

The first-order changes in the Green function can be found as follows:

$$\delta\hat{G}(\omega) = \sum_{\mathbf{k}j} \frac{\delta\psi^l_{\mathbf{k}j\omega}\psi^r_{\mathbf{k}j\omega} + \psi^l_{\mathbf{k}j\omega}\delta\psi^r_{\mathbf{k}j\omega}}{\epsilon_{\mathbf{k}j\omega} - \omega}, \quad (6)$$

which should be used to evaluate the first-order change in the charge density and the dynamical matrix itself.

We now describe our implementation of the method for calculating the vibrational spectra in NiO and MnO. The Neel temperatures in these materials are much lower than their energy gaps and the phonon spectra do not depend dramatically on magnetic ordering. Our main interest is therefore to check the theory in the paramagnetic insulating state. Antiferromagnetic phases can be explored by using spin dependent density functionals like LSDA. It is, for example, well known [21] that the underestimated by the LSDA values of the energy gap and of the magnetic moment can be corrected by the LSDA + U method with U of the order of 8 eV appropriate for these materials. The use of the LSDA + U approximation is equivalent here to a static Hartree-Fock limit of our full frequency resolved theory: the self-energy $\hat{\Sigma}(\omega)$ becomes an orbital-dependent correction to the Kohn-Sham potential V_{eff} expressed via the density matrix of the localized electrons, $n_{\alpha\beta}$. Unfortunately, at the absence of long-range order, LDA necessarily converges to the wrong metallic state. Also LSDA + U makes no sense since it is reduced to the standard LDA. Therefore, the genuine paramagnetic state can be recovered only by using a frequency dependent self-energy. In the Mott

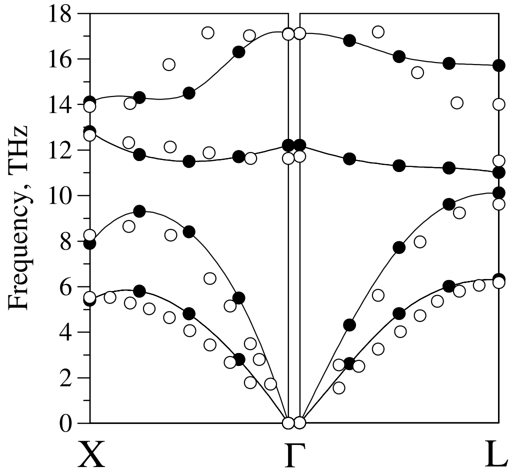

FIG. 1. Comparison between calculated using the present DMFT method (filled circles) and experimental (open circles) phonon dispersion curves for NiO.

TABLE I. Comparisons between Γ-point optical frequencies, energy gap, static dielectric constants ϵ_∞, ϵ_0, and Born effective charges $|Z^*|$ for NiO and for MnO using various methods and experiments.

	NiO					
Method	DMFT	LDA	LSDA	LSDA + U	GW	Expt.
$\omega_{\rm TO}$, THz	12.2	8.9	10.3	12.0	···	11.6$^{\rm a}$
$\omega_{\rm LO}$, THz	17.1	8.9	11.5	17.0	···	17.2$^{\rm a}$
E_g, eV	3.3	0.0	0.5	3.1	3.7–5.5$^{\rm b}$	4.0–4.3$^{\rm c}$
ϵ_∞	6.9	∞	35.7	7.2	···	5.7$^{\rm d}$
ϵ_0	13.6	∞	44.5	14.4	···	12.5$^{\rm h}$
$\lvert Z^*\rvert$	2.3	···	2.2	2.3	···	2.2$^{\rm h}$
	MnO					
Method	DMFT	LDA	LSDA	LSDA + U	GW	Expt.
$\omega_{\rm TO}$, THz	8.9	9.8i	8.6	9.7	···	7.9$^{\rm e}$
$\omega_{\rm LO}$, THz	15.3	9.8i	12.2	15.8	···	15.0$^{\rm e}$
E_g, eV	3.0	0.0	0.9	2.9	4.5$^{\rm f}$	3.6–3.8$^{\rm g}$
ϵ_∞	5.7	∞	10.3	5.9	···	5.0$^{\rm d}$
ϵ_0	16.8	∞	20.7	15.7	···	18.0$^{\rm h}$
$\lvert Z^*\rvert$	2.3	···	2.2	2.3	2.5$^{\rm f}$	2.2$^{\rm h}$

[a] Reference [22]. [b] Reference [23]. [c] Reference [24].
[d] Reference [25]. [e] Reference [26]. [f] Reference [7].
[g] Reference [27]. [h] Estimated from $\omega_{\rm LO}$, $\omega_{\rm TO}$, and ϵ_∞.

insulating limit, it is well described by the Hubbard 1 approximation:

$$\hat{\Sigma}(\omega) = (\omega - \epsilon_d)\hat{I} - \hat{G}_{\rm at}^{-1}(\omega), \tag{7}$$

where we assume that the self-energy operates only between the correlated d electrons located at ϵ_d and $G_{\rm at}(\omega)$ is the atomic Green function for d shell treated in our calculation using the SU(N) symmetry. The use of the Hubbard 1 approximation for $\hat{\Sigma}(\omega)$, (7), assumes no self-consistency loop over hybridization function within DMFT. Here we fix Hubbard U for all the displacements. As a result, the poles of the atomic Green function are fixed and the change in the self-energy due to displacements, $\delta\hat{\Sigma}(\omega)$, vanishes unless $\mathbf{q} = 0$. (In the latter case, variation $\delta\epsilon_d$ of the level ϵ_d appears.)

We now discuss the results of our DMFT calculations which we perform using the LMTO basis and experimental lattice parameters. Figure 1 shows phonon dispersions for NiO along major symmetry directions. A good agreement with experiment [22] can be found for both acoustic and transverse modes. A pronounced softening of the longitudinal optical mode along both ΓX and ΓL lines is seen at the measured data which is in part captured by our theoretical calculation: the agreement is somewhat better along the ΓX direction while the detailed q dependence of these branches shows some residual discrepancies. Table I lists detailed comparisons with the experiment of our Γ-point longitudinal and transverse optical (LO and TO) frequencies. Notably, all values of the frequencies are in good agreement with the measurements.

We can compare the results of these calculations with the paramagnetic LDA, as well as with the antiferromagnetic LSDA and LSDA + U solutions. For the Γ point we list these data in Table I. The paramagnetic LDA does not reproduce the insulating behavior and therefore fails to predict the splitting between the LO and TO modes. Because of metallic screening, it underestimates the vibrations for NiO and predicts them to be unstable for MnO. The spin resolved LSDA solution imposes the existence of long-range magnetic order and does a better job but strongly underestimates the energy gap. As a result, we see an apparent underestimation of the longitudinal optical modes. The LO-TO splitting is also largely underestimated. The transverse optical mode at the Γ point is somewhat better predicted. We also found that acoustic modes are well predicted by the LSDA. These results can be understood since the charge transfer between nearest atoms to a large degree occurs for the longitudinal optical mode only, which strongly affects the screening process by a locally large interaction U. Shortly, when the charge is allowed to flow into the d shell there is not enough repulsion in LSDA resulting in mode softening. The repulsion can be increased if we utilize the LSDA + U method. Really, we have found that this method provides a remarkable hardening of the longitudinal optical modes as seen from Table I. Since the LSDA + U method is simply the Hartree-Fock approximation to the self-energy within our LDA + DMFT theory, we reach a general conclusion that the DMFT based linear response predicts lattice dynamics equally well for both the ordered and disordered magnetic states of these strongly correlated oxides.

To better understand our findings we list in Table I obtained values of the energy gap E_g and calculated values of ϵ_∞ which represent an electronic contribution to the static dielectric constant ϵ_0 as given by the inverse element $1/\epsilon^{-1}(0,0)$ of the full inverse dielectric permittivity matrix in reciprocal space. Table I compares the results of our calculations with the experiment [25]. It is seen that the LSDA result largely overestimates the static dielectric constants. This is partially because the calculated by the LSDA dielectric gaps, which are essentially the charge transfer gaps in NiO and MnO, are much smaller than the experimental ones [24,27]. Also the direct splitting U between the lower and the upper Hubbard d bands is wrong. As a result, the LSDA overestimates the screening of charge fluctuations in both d-p and d-d channels causing the artificial softening of the LO phonons which results in lowering the LO-TO splitting. The latter is well known to be directly proportional to the Born effective charges but inversionally proportional to ϵ_∞.

On the other hand, our calculations with correlations produce much better values of the static dielectric constants as seen from Table I. This is found for both the LSDA + U and the LSDA + Hubbard 1 calculations which we interpret as good approximations to the DMFT solutions for the ordered and disordered magnetic states. We relate such an agreement with the fact that the direct d-d gap is fixed by U, and the charge transfer gap comes out better in the theory. Thus, the local screening of charge fluctuations are treated more appropriately.

In Table I we list for comparison some available results of the calculations based on GW approximation [7,23]. So far there is no general consistency in published values of the energy gaps, and fully self-consistent implementation of the GW is under way. It seems that the GW should predict the gaps closer to the experiment and should have a better description of the dielectric properties. However, the method intrinsically misses the notion of the Hubbard bands and would necessarily fail to describe the paramagnetic insulating regime.

As a final result, we have extracted the values of the Born effective charge Z^* using $\mathbf{q} \to 0$ limit technique [28] and the relationship $\omega_{\mathrm{LO}}^2 - \omega_{\mathrm{TO}}^2 \propto |Z^*|^2/\epsilon_\infty$. Table I shows the comparison between the theoretical and the experimental [22,26] data. The deviation from 2 which for binary oxides is the nominal rigid-ion value of $|Z^*|$ indicates high electronic polarizability. All theoretical values are close to the experimental ones. It is not clear if the agreement for LSDA is accidental due to the error cancellation in underestimating the splitting $\omega_{\mathrm{LO}}^2 - \omega_{\mathrm{TO}}^2$ and overestimating ϵ_∞. In this Letter, however, we emphasize the ability to predict not only the Born charges but *all* the relevant quantities close to the experiment which demonstrates the internal consistency of the new DMFT method.

To summarize, we have developed a new method to study the lattice dynamics of strongly correlated materials at arbitrary wave vector $\mathbf{q}$. We were able to compute the phonons for NiO and MnO in both para- and antiferromagnetic insulating states. We found the results in good agreement with experiments. There are many other challenging problems for which this approach can be useful. Discrepancies between theory and experiment were noticed [29] for the ferroelectric $CaCu_3Ti_4O_{12}$. The electron-phonon interaction in cuprate superconductors is a subject of intensive investigation. The correlation effects can play an important role in the phonon dynamics across the actinide series.

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