Quasiparticles and phonon satellites in spectral functions of semiconductors and insulators: Cumulants applied to full first principles theory and Fröhlich polaron.

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The electron-phonon interaction causes thermal and zero-point motion shifts of electron quasiparticle (QP) energies $\epsilon_k(T)$. Other consequences of interactions, visible in angle-resolved photoemission spectroscopy (ARPES) experiments, are broadening of QP peaks and appearance of sidebands, contained in the electron spectral function $A(k, \omega) = -\Im m G_R(k, \omega)/\pi$, where $G_R$ is the retarded Green’s function. Electronic structure codes (e.g. using density-functional theory) are now available that compute the shifts and start to address broadening and sidebands. Here we consider MgO and LiF, and determine their nonadiabatic Migdal self energy. The spectral function obtained from the Dyson equation makes errors in the weight and energy of the QP peak and the position and weight of the phonon-induced sidebands. Only one phonon satellite appears, with an unphysically large energy difference (larger than the highest phonon energy) with respect to the QP peak. By contrast, the spectral function from a cumulant treatment of the same self energy is physically better, giving a quite accurate QP energy and several satellites approximately spaced by the LO phonon energy. In particular, the positions of the QP peak and first satellite agree closely with those found for the Fröhlich Hamiltonian by Mishchenko et al. (2000) using diagrammatic Monte Carlo. We provide a detailed comparison between the first-principles MgO and LiF results and those of the Fröhlich Hamiltonian. Such an analysis applies widely to materials with infra-red active phonons. We also compare the retarded and time-ordered cumulant treatments: they are equivalent for the Fröhlich Hamiltonian, and only slightly differ in first-principles electron-phonon results for wide-band gap materials.

I. INTRODUCTION

The notion of a single-particle (quasiparticle, or QP) spectrum $\epsilon_k$ for electrons ($k$ is short for all needed quantum numbers - wavevector, band, spin - k, n, σ) underlies much of solid state physics. Justification of the existence of such quasiparticle spectrum relies on experimental results. Optical experiments, combined with theoretical guidance, e.g. the “empirical pseudopotential method” have been used for decades, and have allowed extraction of accurate $\epsilon_k$ from reflectivity data for simple semiconductors. Excitonic effects cause deviation from an independent-particle interpretation, but theory can determine their consequences and help to extract one-electron properties. Angle-resolved photoemission spectroscopy (ARPES) provides a more direct QP spectrum. The data can be approximately related to the rigorously defined one-particle spectral function, obtained from the retarded Green’s function $G(k, \omega)$ as

$$A(k, \omega) = -\frac{1}{\pi} \Im m G_R(k, \omega), \quad (1)$$

where $G_R(k, \omega)$ is the Fourier transform

$$\int dt \exp(i\omega t)G_R(k, t) \quad (2)$$

of the retarded Green’s function

$$G_R(k, t) = -i\langle \{c_k(t), c_k^\dagger(0)\}\rangle \theta(t), \quad (3)$$

and $\{a, b\}$ is an anticommutator. At temperature $T = 0$, the time-ordered (t-O) Green’s function yields also a simple expression,

$$A(k, \omega) = |\Im m G_{t-O}(k, \omega)|/\pi, \quad (4)$$

since the $T = 0$ t-O function has the same imaginary part as $G_R(k, \omega)$, except for a sign change at $\omega = \mu$. 

When the spectral function $A(k, \omega)$ exhibits a strong peak that correlates with the corresponding single-particle theory, this defines a QP energy. The total spectral weight $\int d\omega A(k, \omega)$ is 1, but the QP peak has reduced weight $Z_k < 1$. It is broadened, and accompanied by features at other energies. When clearly differing from a structureless background, these features are called satellites. This has been seen in many photoemission experiments, for example, Ref. [7] for polaron satellites, and Ref. [8] for plasmon satellites. Thus $A(k, \omega)$ contains more information than just the QP energy $\epsilon_k$. Full interpretation is a challenge to theory; progress on plasmon[24,28] and polaron[11] satellites in real semiconductors is occurring.

On the basis of a one-band analysis for metals, Migdal[12] showed that the electron self energy due to phonons has important low temperature dynamical effects, which can be accurately described by a lowest-order self energy diagram $\Sigma_M$. Vertex corrections can be omitted because of the small ratio $\omega_{\text{ph}} / E_F$ of phonon energies to the Fermi energy. Even though this argument that allows to neglect vertex corrections does not strictly apply in semiconductors, we will use the term “Migdal” to indicate the Migdal formula, $\Sigma_M$, given later as Eq. (5), where it is labeled $\Sigma_{\text{DM}}$, referring to earlier works on insulators by Fan in the fifties. Using Dyson’s equation, the corresponding Green’s function is

$$G_D(k, \omega) = G_0(k, \omega) + G_0(k, \omega)\Sigma_M(k, \omega)G_D(k, \omega).$$

(5)

When inserted into Eq. [1], it gives a spectral function which we will call “Dyson-Migdal”, $A_{\text{DM}}$. Given the success of Migdal theory in metals and the expected success of low order perturbation theory for most electron-phonon problems, it is embarrassing to realize[15–17] that $A_{\text{DM}}(k, \omega)$ often agrees poorly with measured $A(k, \omega)$. Typically, only one distinct satellite is found (somewhat misplaced) in the side-band spectrum, while in reality several satellites are possible, corresponding to emission of several phonons. Even worse, the QP peak is misplaced.

An alternative approach, also approximate, involves a cumulant treatment (see e.g. Refs. [19–22] and pp. 410–415 of Ref. [2]). This will be denoted as $G_C$ for the Green’s function, and $A_C$ for the spectral function. The cumulant was advocated for describing plasmon satellite effects in metals by Steiner et al.9 and Hedin[23]. For electron-phonon effects, the earliest use was by Dunn[15] for the polaron spectral function. Gunnarsson et al.10 introduced the cumulant method for electron-phonon effects in metals. Verdi et al.11 applied the cumulant method to doped semiconductors, where both plasmon and phonon effects occur. Here we apply the cumulant method to undoped semiconductors with electron-phonon renormalization but no dynamical electron-electron coupling.

To further motivate the interest to work with the cumulant approach instead of the Dyson-Migdal one, consider Fig. 1 which illustrates where the QP peak appears in various treatments of the Fröhlich polaron problem. Lowest-order Rayleigh-Schrödinger perturbation theory puts the renormalized polaron energy below the conduction band minimum by $\omega L_0$, where $\alpha$ is the Fröhlich coupling constant. An accurate high-order treatment[23] gives a surprisingly similar answer, shown as the blue squares on the graph. This is where the QP peak of the spectral function should be located. If the Migdal self energy $\Sigma_M$ is evaluated at $\omega = \epsilon_k$, the unperturbed energy, the corresponding energy shift $\Delta\epsilon_k = \Sigma_M(0, \epsilon_k)$ agrees with the Rayleigh-Schrödinger result $-\alpha \omega L_0$. However, the actual QP peak of the spectral function $A_{\text{DM}}$ is located at a fairly different energy, shown by the red circles on the graph. The cumulant method used in the present paper puts the QP peak exactly on the Rayleigh-Schrödinger line, close to the correct polaron answer. The cumulant method also greatly improves the position of the first satellite peak, as will be shown later. It also gives additional peaks, corresponding to multiphonon excitations. However, they differ in location and strength from the other peaks in the accurate Fröhlich spectral function.

Another improvement given by the cumulant method is a much more reasonable value of the QP spectral weight $Z$, defined later in Eq. (15) and shown in Fig. 2.

Since the characteristic energy of plasmons is much bigger than that of phonons, the resolution needed to see them in photoemission experiments has been available for many years. The valence photoemission spectra of alkali metals, that exhibit multiple plasmon satellite structures, was modeled from first principles by Aryasetiawan et al. using a cumulant treatment. More recently, Kheifets et al. and Guzzo et al. did ARPES for valence electrons in Si. They observed plasmon satellites caused by screened Coulomb interaction. Their calcu-
Electron-phonon interaction (EPI) effects are ubiquitous in solids, but were not seen in ARPES until improved resolution became available. In metals, temperature shifts of photoemission linewidths were seen for surface states in Cu, and for several other materials. The homogeneous electron gas has also been studied using the cumulant approach, as well as more recent contributions, such as the Monte Carlo approach to second order, which provides a cumulant calculation of the quasiparticle spectral weight. The literature on large polarons has focussed on models such as the Fröhlich Hamiltonian, generally ignoring the existence of multiple phonon branches, non-parabolic electronic bands, Debye-Waller, and interband effects. We advocate unification of the separate skills of polaron and energy-band communities. This has started, with the above-mentioned understanding of the LO-phonon role in first-principles calculations, as well as the first-principles approach to the Fröhlich vertex developed by Sjakste et al. and Verdi and Giustino.

Beyond the computation of quasiparticle shifts, first-principles studies of spectral functions, side bands and satellites have also appeared. Cannuccia and Marin showed that optical data for diamond and polyethylene contain subgap EPI effects, as well as more recent contributions, such as the Monte Carlo approach to second order, which provides a cumulant calculation of the quasiparticle spectral weight. The literature on large polarons has focussed on models such as the Fröhlich Hamiltonian, generally ignoring the existence of multiple phonon branches, non-parabolic electronic bands, Debye-Waller, and interband effects. We advocate unification of the separate skills of polaron and energy-band communities. This has started, with the above-mentioned understanding of the LO-phonon role in first-principles calculations, as well as the first-principles approach to the Fröhlich vertex developed by Sjakste et al. and Verdi and Giustino.

The focus has mostly been on the quasiparticle shift in simple solids, and occasionally on the quasiparticle broadening. Polarons, by contrast, have been studied for a long time using high-order perturbative treatment of the singular Fröhlich first-order matrix element, with no second or higher-order matrix elements, and simplified model band structure. When the Fröhlich coupling constant $\alpha$ exceeds $\approx 5$, nonperturbative corrections start to be needed, and eventually small polarons may form in real materials where the polaron radius in the continuum approach would be comparable or smaller than the interatomic distance. Also, defects or higher than harmonic lattice displacement terms cannot be ignored in real materials. Only recently was it noticed that first-principles studies of semiconductors had incorrectly ignored nonadiabatic aspects familiar in polaron literature for the quasiparticle energy shift (also sometimes referred to as renormalization) due to LO phonons in infrared-active semiconductors. Perturbation theory had previously been simplified by omission of $\pm \omega Q$ from denominators. Because of the $1/q$ divergence of the Fröhlich coupling, LO phonon contributions cause unphysical divergences (3D-integral of $1/q^4$ at small $q$) phonon wavevectors) if the $\pm \omega Q$ pieces are omitted.

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The current paper deals with the zero-temperature spectral function $A(k, \omega, T = 0)$, for states $k$ at band extrema near the gap of two real insulators, MgO and LiF, arising from EPI effects. The Migdal method is used for $\Sigma(k, \omega)$ including, for polar EPI’s, the $\pm \omega_q$ in energy denominators, see Eqs. (6)–(10). The Migdal level of perturbation theory assumes that the Fröhlich coupling constant $a$ is not too big. We compute the spectral function both at the Dyson-Migdal ($A_{DM}(k, \omega)$) and cumulant ($A_C(k, \omega)$) levels, and show that the cumulant version is physically more sensible.

We first summarize the theoretical background for (a) computation of self energies, and (b) spectral functions. Then we consider the Fröhlich Hamiltonian, and discuss results for several values of the coupling constant $a$. Subsequently we calculate the self energy and the spectral function, for the top of the valence band and bottom of conduction band of MgO and LiF, using $ab$ initio density functional perturbation theory (DFPT) calculations with the code ABINIT[75,79] to determine phonons and their coupling with electrons. We consider, for these states, the Dyson-Migdal (D-M) approach, as well as different flavors of the cumulant approach. Given the small phonon frequencies with respect to the wide gap of these materials, the results are essentially identical for the different cumulant approaches, while the D-M approach gives qualitatively very different results. This calls for a reconsideration of the results based on the D-M approach given in Refs. [77,11] and [58].

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Quantitative tests for EPI effects in non-metals treated with a cumulant approach are almost nonexistent. We are only aware of the above-mentioned model calculations for the Fröhlich Hamiltonian by Dunn[11] and first-principles study of TiO$_2$ by Verdi et al.[111]

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The Hartree atomic unit system is used throughout ($\hbar = m_e = e = 1$). Starting from now, we will use the more explicit notations $k$ for wavevectors and $n$ for bands, instead of $k$. Spin is irrelevant in this article. The self energy of an unperturbed state, labelled by wavevector and band, includes two contributions at the lowest order of perturbation theory (quadratic in the strength of the EPI), namely, the Fan self energy and the Debye-Waller self energy:

$$\Sigma(k\mu, \omega) = \Sigma^{FAH}(k\mu, \omega) + \Sigma^{DW}(k\mu). \tag{6}$$

The Debye-Waller self energy (see its expression in Refs. [33,53]) is static and real. On the contrary, the Fan self energy is dynamical. In matrix notation, the Fan self energy is given by $\Sigma = iG_{tO}$, where $G$ is the electron propagator, $\Gamma$ is the vertex, and $D$ is the phonon propagator. As soon as $G$ is calculated, the vertex is approximated as $\Gamma = 1$. Approximating the electronic Green’s function by its non-interacting counterpart, $G = G^{(0)}$, e.g. Kohn-Sham Green’s function without electron-phonon corrections, corresponds to a non-self-consistent treatment, and gives the standard result for the retarded Fan self energy:

$$\Sigma^{FAH}(k\mu, \omega) = \frac{1}{N_q} \sum_{q_j} \sum_{n'} |\langle \mu|H_{q_j}^{(1)}|k+q_n'\rangle|^2 \times \left[ \frac{n_{q_j} + 1 - f_{k+q_n'}}{\omega - \varepsilon_{k+q_n'} - \varepsilon_{q_j} + i\eta} + \frac{n_{q_j} + f_{k+q_n'}}{\omega - \varepsilon_{k+q_n'} + \varepsilon_{q_j} + i\eta} \right]. \tag{7}$$

In this expression, contributions from phonon modes with harmonic phonon energy $\omega_{q_j}$ and occupation number $n_{q_j}$, are summed for all phonon branches, labelled $j$, and wavevectors, labelled $q_j$, in the entire Brillouin zone. The latter is discretized, with $N_q$ indicating the number of wavevectors in the sum. The limit for infinite number of wavevectors is implied. Contributions from intermediate electronic states $|k+q_n'\rangle$ with electron energy $\varepsilon_{k+q_n'}$ (not renormalized by phonons) and occupation number $f_{k+q_n'}$ are summed for all bands $n'$ (valence and conduction). $H_{q_j}^{(1)}$ is the self-consistent change of potential due to the phonon labelled $q_j$. Eq. (7) is also the Migdal result $\Sigma_M$.

The t-O Fan self energy is obtained from the above retarded self energy by multiplying the infinitesimal quantity $\eta$ by sign($\varepsilon_{k+q_n'} + \omega_{q_j} - \mu$) in the first denominator, and by sign($\varepsilon_{k+q_n'} - \omega_{q_j} - \mu$) in the second denominator. The retarded self energy has all poles below the real axis, while the poles of the t-O self energy are below the real axis if the pole is above the chemical potential energy $\mu$, and above the real axis if the pole is below the chemical potential energy $\mu$.

In the present article, we will work with semiconductors at zero temperature, in which case the phonon occupation numbers vanish, and the electron occupation
numbers $f_{k+q'\nu}$ are either one, for the valence states, or zero, for the conduction states. There are separate contributions to the Fan self energy from the intermediate states $|k+q\nu'angle$ in the conduction bands (labelled ‘un’ for unoccupied) and in the valence band (labelled ‘oc’ for occupied). No matter whether the initial state $|kn\rangle$ is from the valence or the conduction band, both contributions occur,

$$
\Sigma_{\text{Fan}}(kn, \omega) = \Sigma_{\text{un}}(kn, \omega) + \Sigma_{\text{oc}}(kn, \omega).
$$

Explicit equations are

$$
\Sigma_{\text{un}}(kn, \omega) = \frac{1}{N_\text{q}} \sum_{q} \sum_{n'} \delta(E_{kn} - E_{kn'} - \omega_{qj} + i\eta) \langle [kn|H_j^{(1)}|k + qn'] \rangle^2
$$

for the intermediate unoccupied state contribution to the self energy (be it retarded or t-O), and

$$
\Sigma_{\text{oc}}(kn, \omega) = \frac{1}{N_\text{q}} \sum_{q} \sum_{n'} \delta(E_{kn} - E_{kn'} - \omega_{qj} + i\eta) \langle [kn|H_j^{(1)}|k + qn'] \rangle^2
$$

for the intermediate occupied state contribution to the self energy (for the t-O one, the sign of $i\eta$ is changed, which changes the imaginary part of the self energy, but not the real part). The imaginary part of the retarded self energy is always negative, while the t-O one is negative above the chemical potential, and positive below it. Only the retarded self energy satisfies Kramers-Kronig relationships.

For semiconductors with infrared-active phonons, the intraband ($n' = n$) contribution with small-$q$ LO phonons (the Fröhlich problem) gives the most important dynamical features for the frequency range near the bare electronic energy ($\omega \approx \epsilon_{kn}$), due to the combination of small-$q$ diverging matrix element $\langle kn|H_j^{(1)}|k + qn' \rangle \rightarrow C_n \delta_{nn'} / q$, see Ref. 57 and small denominator ($\omega \approx \epsilon_{kn} \approx \epsilon_{k+qn}$) in Eqs. (9-10).

III. QUASIPARTICLES AND SPECTRAL FUNCTION

The second-order self energy $\Sigma(kn, \omega)$ is the basis of different approximations for the quasiparticle shift and the spectral function. In the Rayleigh-Schrödinger (RS) approximation, the new quasiparticle energy $E_{kn}^{\text{RS}}$ is shifted from its initial value $\epsilon_{kn}$ by the real part of the self energy evaluated at $\epsilon_{kn}$:

$$
E_{kn}^{\text{RS}} = \epsilon_{kn} + \Re\Sigma(kn, \omega = \epsilon_{kn}).
$$

The spectral function $|\Im m G(kn, \omega)| / \pi$ (either t-O or retarded $G$, since we take $T = 0$) has dynamical effects beyond Rayleigh-Schrödinger. In the Dyson-Migdal (D-M) approach, the spectral function obtained from the self energy is

$$
A_{\text{DM}}(kn, \omega) = \frac{1}{\pi} |\Im m G_D(kn, \omega)|
$$

\[= \frac{1}{\pi} |\Im m \Sigma(kn, \omega)|
\]

\[= \frac{(1/\pi)|\Im m \Sigma(kn, \omega)|}{(\omega - \epsilon_{kn} - \Re\Sigma(kn, \omega))^2 + (\Im m \Sigma(kn, \omega))^2}.
\]

There is typically a QP peak at $\omega = E_{kn}^D$ where $\omega - \epsilon_{kn} + \Re\Sigma(kn, \omega) = 0$ (i.e. where the first term in the denominator of Eq. (12) vanishes). This assumes small values of $\Im m \Sigma$ near $\omega = E_{kn}^D$. If $\Im m \Sigma$ is not small at $E_D$, the QP peak can be strongly broadened. The value of $E_D$ is usually shifted from $E_{kn}^{\text{RS}}$ (Eq.(11)) by a non-negligible $\omega$-dependence of $\Re\Sigma(kn, \omega)$. An additional possible slight shift of the QP peak in Eq.(12) can occur if the $\omega$-dependence of $\Im m \Sigma$ is not negligible at $E_D$. Eq. (12) usually also gives one broad satellite mainly above the quasi-particle peak (for the conduction states), or below it (for the valence states).

A QP part of the spectral function, in Dyson-Migdal theory, can be separated out by Taylor expanding $\Sigma_{\text{Fan}}$ around $\omega = E_{kn}^D$, keeping only the constant term in the imaginary part and both constant and linear terms in the real part. The answer is

$$
A_{\text{DM}}^{\text{QP}}(kn, \omega) = \frac{Z_{kn}^D}{\pi} \frac{Z_{kn}^D}{\pi} \frac{\Gamma_{kn}^D}{\omega - E_{kn}^D + (\Gamma_{kn}^D)^2}
$$

where the QP energy is

$$
E_{kn}^D = \epsilon_{kn} + \Re\Sigma(kn, \omega = E_{kn}^D),
$$

the quasiparticle weight $Z_D$ is

$$
Z_{kn}^D = \left(1 - \Re\frac{\partial\Sigma(kn, \omega)}{\partial\omega} \Big|_{\omega = E_{kn}^D} \right)^{-1},
$$

and the QP broadening is

$$
\Gamma_{kn}^D = Z_{kn}^D |\Im m \Sigma(kn, \omega = E_{kn}^D)|.
$$

In case $T = 0$ and the imaginary part of the self-energy vanishes at the QP energy, Eqs. (14) and (15) are the exact location and weight of a scaled Dirac delta peak $Z_{kn}^D \delta(\omega - E_{kn}^D)$.

Often (16) Eq. (14) is linearized to find an approximate quasiparticle energy and the related weight from quantities defined at the bare eigenenergy $\epsilon_{kn}$:

$$
E_{kn}^{\text{Dlin}} = \epsilon_{kn} + Z_{kn}^{\text{Dlin}} \Re\Sigma(kn, \omega = \epsilon_{kn}),
$$

with

$$
Z_{kn}^{\text{Dlin}} = \left(1 - \Re\frac{\partial\Sigma(kn, \omega)}{\partial\omega} \Big|_{\omega = \epsilon_{kn}} \right)^{-1}.
$$
The Lehmann representation of the spectral function is derived from Eqs.(13) using the exact eigenstates $|m\rangle$, of energy $E_m$, of the full Hamiltonian,

$$A(kn, \omega) = \sum_{m',m} \frac{e^{-\beta E_m}}{Z} \left[ (m'|c_{kn}^+|m\rangle)^2 \delta(\omega - E_{m'} + E_m) + (m'|c_{kn}|m\rangle)^2 \delta(\omega + E_{m'} - E_m) \right].$$

(19)

where $Z$ is the partition function, $\Sigma_m \exp(-\beta E_m)$ and $\beta$ is $1/k_B T$. Only $T = 0$ is directly relevant to the computations of this paper, but the $T > 0$ properties are also important and interesting. From Eq.(19) it is clear that $A(kn, \omega) \geq 0$ at all $\omega$, and the integrated spectral weight ($\int d\omega A(kn, \omega)$) is 1. The QP part (Eq.(13)) has total weight $Z^D$, which must therefore be less than 1. The non-QP part $A - A_{QP}$ has the rest of the spectral weight.

There is an interesting property of the first moment

$$\int_{-\infty}^{\infty} d\omega A(kn, \omega) = \langle \{c_{kn}, H\}, c_{kn}^+ \rangle.$$

(20)

For noninteracting electrons, the right-hand side of Eq.(20) is the band energy $\epsilon_{kn}$. If the only interaction is with phonons, the right-hand side has an extra piece, $\langle \{c_{kn}, H_{c-p}\}, c_{kn}^+ \rangle$. Terms in the electron-phonon interaction $H_{c-p}$ which have odd powers of lattice displacement do not contribute. The even powers do, however, and the total right hand side of Eq.(20) is $(kn|H)|kn\rangle$ where $\langle H\rangle$ is the thermal average of the vibrating one-electron Hamiltonian. This is exactly a Debye-Waller shifted single particle energy, both zero-point and thermal if $T > 0$. If only the leading second-order term in a vibrational Taylor expansion is kept, the answer is $\epsilon_{kn} + \Sigma_{DW}(kn)$, with only the Debye-Waller part of Eq.(4). It is interesting that an observable (in principle) property can separate the Debye-Waller from the Fan effects, given that translational invariance forces a partial cancellation and indicates an underlying connection between these terms.

Although the quasiparticle energy from the D-M spectral function for the Fröhlich problem does not occur at the right place and the D-M quasiparticle spectral weight is quite bad, as shown by Figs. 1 and 2, the integral of the D-M spectral function is correctly 1, and its first moment is correctly $\epsilon_{kn}$ for the Fröhlich problem which has no 2-phonon matrix element and therefore no D-W term.

IV. CUMULANT

The cumulant expansion is an alternative to the usual Dyson diagrammatic perturbation theory. It derives from an exponential representation of the Green’s function $G(kn, t)$, either retarded or t-O, in the time domain:

$$G_C(kn, t) = G_0(kn, t)e^{C(kn, t)}.$$

(21)

To lowest order, it treats the Fan diagram, Fig. 3 (a), exactly, and higher-order diagrams such as (b) and (c), approximately.

Different methods are used to derive the cumulant $C(kn, t)$ from the self energy, including identification of the terms of the same power of the interaction in a diagrammatic expansion of the left- and right-hand side of Eq.(21). In the case of one isolated electronic level (without dispersion), the cumulant approach gives the exact result using only a second-order self energy. Among others, Langreth, Hedin, Gunnarsson et al., Aryasetiawan et al., Guzzo et al. and Kas et al. examined, developed and applied the cumulant expansion.

Prior cumulant work supposed decoupling between empty and occupied states, and worked in a t-O formulation. In a recent paper, Kas et al. considered a cumulant expansion of the retarded Green’s function. In the case of metals, they find that the retarded version correctly includes recoil effects that mix particle and hole states, while these do not appear within the existing cumulant approaches based on t-O Green’s functions where particle and hole states are treated separately. Their equations, applied to the EPI self energy (including Fan and Debye-Waller contributions), are

$$A_C^R(kn, \omega) = -\frac{1}{\pi} \Im G_C^R(kn, \omega),$$

(22)

$$G_C^R(kn, \omega) = \int_{-\infty}^{\omega} e^{-i\omega t} G_C^R(kn, t)dt,$$

(23)

$$C_C^R(kn, t) = -i\theta(t)e^{-i(\epsilon_{kn} + \Sigma_{DW}^D)}e^{C^R(kn, t)},$$

(24)

$$\beta_R(kn, \omega) = \frac{1}{\pi} \Im [\beta M_{fan}(kn, \omega + \epsilon_{kn})].$$

(26)

Eq.(24) shows that the static Debye-Waller self energy $\Sigma_{DW}^D$ shifts (in frequency) the whole spectral function with respect to $\epsilon_{kn}$. The retarded character of the Green’s function is present in Eq.(24), where both unoccupied and occupied states contribute (compare with Eqs.(33) and (35), given later). Another effect of the retarded character of this cumulant is the limits of frequency integrals in Eq.(25) (compare with Eqs.(32) and (34)).
The evaluation of Eq. [25] might appear delicate due to possible numerical problems associated with the square of the frequency in the denominator. However, the numerator and its first derivative also vanish for ω = 0. The same Eq. [25] also shows that the cumulant and its first time derivative vanish at t = 0, from which one deduces that the integral of the spectral function \( A_R^k(n, ω) \) over all frequencies is 1, while its first moment is equal to \( ε_{kn} + \Sigma_{PW}^{DW} \). These properties agree perfectly with the exact results of the previous section.

Moreover, for the EPI, the phonon density of states (DOS) from acoustic modes vanishes quadratically at energy. Unlike the retarded cumulant, this version of the t-O cumulant does not vanish at t = 0, nor does its time-derivative, which means that the spectral function is not normalized to 1, and its first moment is changed by the dynamical contribution. Corresponding expressions for the holes are also presented in Ref. [77].

\[
C_h^{t-O}(k, n, t) = \int_{-∞}^{μ-ε_{kn}} β_h^{t-O}(k, n, ω)e^{-iωt}\Re 1 \left( \frac{1}{(ω + iδ)^2} \right) dω - it\Sigma_{PW}(k, n, ω) + \frac{∂\Sigma_{PW}(k, n, ω)}{∂ω} |_{ω=ε_{kn}},
\]

(34)

\[
β_e^{t-O}(k, n, ω) = \frac{1}{π} |\Im m\Sigma_{PW}(k, n, ω + ε_{kn})|.
\]

(35)

Note the reduced range of the integral, as well as the selection of part of the self energy in the β factor. By contrast, the contributions that are either constant in time or linear in time are computed from the whole self energy. Unlike the retarded cumulant, this version of the t-O cumulant does not vanish at t = 0, nor does its time-derivative, which means that the spectral function is not normalized to 1, and its first moment is changed by the dynamical contribution. Corresponding expressions for the holes are also presented in Ref. [77].

\[
C_h^{t-O}(k, n, t) = \int_{-∞}^{μ-ε_{kn}} β_h^{t-O}(k, n, ω)e^{-iωt}\Re 1 \left( \frac{1}{(ω + iδ)^2} \right) dω - it\Sigma_{PW}(k, n, ω) + \frac{∂\Sigma_{PW}(k, n, ω)}{∂ω} |_{ω=ε_{kn}},
\]

(34)

\[
β_h^{t-O}(k, n, ω) = \frac{1}{π} |\Im m\Sigma_{PW}(k, n, ω + ε_{kn})|.
\]

(35)

Slightly different versions of the t-O cumulant arise from the replacement of the full Fan self energy and its derivative, in the last two terms of Eqs. [32] and [34], by their unoccupied and occupied counterparts, respectively, as in Ref. [22] (see Eq. [36]), or the replacement of its derivative only, as in Refs. [10] and [77] (see Eqs. 3.32 and 3.33 of Ref. [77]). In both cases, the normalization is brought back. Our computations for MgO and LiF have such large band gaps that the differing limits of integration in Eqs. [31], [32] and [34] have negligible consequences. Similarly, the function \( β_{PW}(k, n = c) \) is almost identical to \( β_e^{t-O} \) and \( β_R(k, n = v) \) is almost identical to \( β_h^{t-O} \), in the relevant range of ω-integration where the denominator \( ω^2 \) is small. The different versions of cumulant methods are thus sufficiently similar that only retarded cumulant results are presented here.

In Eq. [21], or equivalently Eq. [24], the exponential can be Taylor-expanded: the Green’s function and spectral function in the time domain are the sum of the product of the independent-electron contribution multiplied by powers of the cumulant, the latter being a linear functional of the imaginary part of the self energy. In the frequency domain, this creates a satellite series coming from repeated convolution in frequency of the undressed particle spectral function (a Dirac delta) by the “satellite spectral function” \( A^5 \) (See Eqs. 8, 13, and 14 of Ref. [9] or Eqs. 3, 4, and 6 of the supplemental materials of Ref. [11]). Supposing \( A^5 \) to be also a Dirac delta (as in the Lundqvist model Hamiltonian), one obtains for the spectral function a Poisson distribution of Dirac function satellites, each being spaced by the characteristic bosonic satellite energy. More generally, supposing the imaginary part of the self-energy to be non-zero only for positive frequencies beyond a given threshold, the threshold for each satellite contribution will be determined by the self-energy threshold multiplied by the order of the satellite.

In the next section, one will see such an effect in the case of the Fröhlich Hamiltonian.

When the imaginary part of the self energy has contributions at both negative and positive frequencies, this
simple picture is lost, unless the cumulant is clearly dominated by one of these. In the case of the first-principles EPI for wide-gap insulators, the self energy has indeed both negative and positive contributions. However, only one of these contributions will dominate for wide-gap insulators, as will be seen later.

V. FRÖHKLICH HAMILTONIAN SELF-ENERGY

The relationship between the Fröhlich coupling and first-principles calculations has been established in Refs. 68 and 69 in the general case of several electronic bands, several phonon branches, as well as anisotropic Born effective charge tensor and dielectric tensor. Here, we consider the simple original Fröhlich Hamiltonian, corresponding to the following hypotheses: (1) Only one isotropic electronic parabolic band (we will first treat the conduction band), with a minimum at \( k = 0 \). We choose \( \epsilon_{k=0,c} = 0 \), and use parabolic dispersion governed by the effective mass \( m^* \). (2) Only one LO-phonon branch with constant phonon frequency \( \omega_{LO} \). (3) Isotropic Born effective charge \( Z^* \), isotropic electronic (optical) dielectric constant \( \epsilon_{\infty} \), and thus, isotropic low-frequency dielectric constant \( \epsilon_0 \).

Only intraband terms \( n' = n \) are present, thus, the general \( g_{n'n'}(k, q) = \langle k|n|H_{q}^{(1)}|k + qn'\rangle \) reduces to \( g_{nn'}(k, q) = g_q \delta_{nn'} \) for \( j = LO \), with

\[
g_q = \frac{i}{q} \frac{4\pi \omega_{LO}}{\Omega_0} \frac{1}{2} \left( \frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_0} \right) \frac{1}{\sqrt{\omega/\omega_{LO} - 1}}, \tag{36}
\]

where \( \Omega_0 \) is the volume of the primitive cell.

In computing the self energy, the constant Debye-Waller shift is neglected. This might seem a strong approximation. However, hypothesis (2) implies the neglect of the Fan term from the acoustic modes as well, and it is known that the acoustic mode Fan contributions and the Debye-Waller contributions cancel each other in the vanishing-\( q \) limit. Furthermore, the LO-phonon Fan term dominates, due to the integrable divergence mentioned at the end of Sec. II.

The expression for the Fröhlich self energy is easily found, see e.g. Ref. 19, but is presented here as well, for convenience and comparison with the first-principle results. The zero-temperature formula for the Fan self energy of the (Fröhlich) electron state at the bottom of the conduction band \( (k = 0) \) comes from Eq. (9):

\[
\Sigma_{F,c}(k = 0, \omega) = \frac{1}{N_q} \sum_q \frac{|g_q|^2}{\omega - \epsilon_q - \omega_{LO} + i\eta} \tag{37}
\]

The intermediate electron energy \( \epsilon_q \) becomes \( q^2/2m^* \) in the parabolic band with effective mass approximation. Using the Debye sphere for the Brillouin zone, the equation becomes

\[
\Sigma_{F,c}(0, \omega) = \int_0^{q_D} dq \frac{\Omega_0}{(2\pi)^3} \frac{4\pi q^2 |g_q|^2}{\omega - q^2/2m^* - \omega_{LO} + i\eta \omega} \tag{38}
\]

Provided the electronic energy on the boundary of the Debye sphere is much bigger than \( \omega_{LO} \), the upper limit \( q_D \) can be safely extended to infinity. For \( q_D \to \infty \), this gives

\[
\Re \Sigma_{F,c}(\omega) = -\frac{\alpha \omega_{LO}}{\sqrt{1 - \omega/\omega_{LO}} \omega_{LO}} \theta(\omega_{LO} - \omega), \tag{39}
\]

\[
\Im m \Sigma_{F,c}(\omega) = -\frac{\omega_{LO}}{\sqrt{\omega/\omega_{LO} - 1}} \theta(\omega - \omega_{LO}), \tag{40}
\]

where the Fröhlich coupling constant \( \alpha \) is

\[
\alpha = \left( \frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_0} \right) \left( \frac{m^*}{2\omega_{LO}} \right)^{1/2}. \tag{41}
\]

Above \( \omega_{LO} \), the self energy is purely imaginary, while below \( \omega_{LO} \), it is purely real. Both are negative and diverge like an inverse square root of the frequency around \( \omega_{LO} \).

For the valence band, with the eigenenergy of the top of the valence band now taken as zero, the corresponding retarded self energy is

\[
\Re \Sigma_{F,v}(\omega) = +\frac{\alpha \omega_{LO}}{\sqrt{1 + \omega/\omega_{LO}}} \theta(\omega + \omega_{LO}), \tag{42}
\]

\[
\Im m \Sigma_{F,v}(\omega) = -\frac{\omega_{LO}}{\sqrt{-\omega/\omega_{LO} - 1}} \theta(-\omega - \omega_{LO}). \tag{43}
\]

In the t-O case, the hole self energy has imaginary part of opposite sign. For a given material with well-defined dielectric constant and LO frequency, the coupling constant \( \alpha \) from Eq. (41) has different values for electron and hole polarons, due to differing effective masses.

In Secs. VII and VIII dealing with first-principles calculations, we will maintain a small finite broadening factor \( \eta \), of order 0.1\( \omega_{LO} \), for numerical reasons. Thus the self-energy functions, Eqs. (39) and (43), will not retain their inverse-square-root shape. Eqs. (39) and (40) and their broadened versions are represented in Fig. 4.

The self energies in Eqs. (39)-(43) were derived in lowest order perturbation theory. They include only the Fan diagram, without vertex corrections. Calculations of self energies at higher orders have been performed for the Fröhlich Hamiltonian, see e.g., Refs. 15 and 19. For values of \( \alpha \) in the range considered in the present paper, those higher-order corrections to the D-M version of the quasiparticle shift are small, consistent with Migdal.

Calculations using these formulas for \( \Sigma_F \) and the corresponding spectral functions \( \Delta_{DM} \) and \( \Delta_C \), are discussed in the next section, and plotted in Figs. 5, 6.

VI. FRÖHKLICH HAMILTONIAN 
QUASIPARTICLE ENERGY AND SPECTRAL FUNCTION

The Rayleigh-Schrödinger approximation Eq. (11) with the self energy Eq. (39), gives the quasiparticle peak at \( E_{QP}^{RS} = -\alpha \omega_{LO} \) for the Fröhlich Hamiltonian, at \( k = 0 \) with \( \epsilon_{k=0,c} = 0 \). This is the standard Fröhlich result.
Physically, this satellite ought to start at the quasiparticle peak, but the quasiparticle peak differs more and more between the two, with the cumulant version staying at the RS answer $-\omega_{LO}$, albeit small, has an impact on the threshold at which it becomes impossible to distinguish the satellites from the overall smooth behaviour. Indeed, this broadening factor is multiplied by the order of the satellite in the repeated convolution of the undressed particle spectral function mentioned in Sec. IV.

These cumulant results globally agree with the previous cumulant-based study by Dunn [15] for $\alpha = 2, 4, 6$. He worked, however, at finite temperature, and also included the next order of perturbation theory in his calculations of the self energy. Higher orders of perturbation theory tend to sharpen features of the spectral function. In the case of a model core-electron spectrum, for which the exact solution is known [19], the next order of perturbation theory improves significantly the position of the peak, and sharpens it with respect to a first-order self-consistent treatment. A first-order non-self-consistent treatment also gives a sharper plasmon satellite than the first-order self-consistent treatment, albeit located at nearly the same too low energy $\omega_{LO}$. 

By contrast, it is higher by $\omega_{LO}$ than the bare band energy $\omega = \epsilon_k(0) = \Omega_{\omega}$. By contrast, it is higher by $\omega_{LO}$ than the quasiparticle peak in the cumulant method, corresponding to states that combine the dressed quasiparticle with one LO phonon.
grammatic Monte Carlo (MC) calculations of Mischenko et al.\textsuperscript{83} apparently the best reference results available at present. However, the MC results do not show the second and third satellites and instead develop a satellite in the range from 3.5 to 4.0 \( \omega_{LO} \) if \( \alpha \) is larger than one. For values of \( \alpha \) larger than 4, another satellite appears in the range 8.0 ... 9.0 \( \omega_{LO} \). As MC results for optical \( \sigma(\omega) \) compare well with other approaches,\textsuperscript{83} we believe that the cumulant approach for \( A(k, \omega) \) has some errors for \( \omega \) beyond the first satellite. The physical reason for the disappearance of the second and third multiphonon peaks, and the appearance of other peaks, has been discussed in Ref.\textsuperscript{83} The new peaks relate to so-called “relaxed excited states”, not treated by the lowest order cumulant approach, that dominate the spectral function in the energy range beyond the first phonon threshold.

Let us analyze the behavior of the quasiparticle peak in the D-M case in more detail, in the case without any numerical broadening. The quasiparticle energy is found from

\[
E_{QP}^D = \Re \Sigma(E_{QP}^D). \tag{44}
\]

Using Eq.(38) for electron states gives a cubic equation,

\[
\alpha^2 = \left( \frac{E_{QP}^D}{\omega_{LO}} \right)^2 - \left( \frac{E_{QP}^D}{\omega_{LO}} \right)^3; \quad (E_{QP}^D < 0). \tag{45}
\]

For all \( \alpha \), this has one negative real root; \( E_{QP}^D \sim -\alpha \omega_{LO} \) for small \( \alpha \) and \( E_{QP}^D \sim -\alpha^2/3 \omega_{LO} \) for large \( \alpha \). This agrees with Fig.6 (red circles). For small \( \alpha \), the leading correction to RS is

\[
E_{QP}^D \approx -(\alpha - \alpha^2/2)\omega_{LO} \tag{46}
\]

The D-M quasiparticle energy Eq.(44) corresponds to the intersection of the \( \Re \Sigma(\omega) \) function with the straight \( \omega \) line, as shown in Fig.6 As shown in Fig.1 the second-order Rayleigh-Schrödinger answer \( E_{QP}^{RS} = -\alpha \omega_{LO} \) is not the self-consistent \( \Sigma_M = G_D \), not the D-M-Migdal solution, see Ref.\textsuperscript{18}. The Fröhlich spectral function \( A = -3m G_R(\omega)/\pi \), in D-M approximation, has two parts. The quasiparticle part is \( Z^D \delta(\omega - E_{QP}^D) \), where \( Z^D = 1/(1-d\Sigma/d\omega) \) is evaluated at \( \omega = E_{QP}^D \). To lowest order, the quasiparticle weight \( Z^D \approx 1 - \alpha/2 \). At large \( \alpha \), \( Z^D \) tends asymptotically to 2/3, but the linearized weight, Eq.(18) is \( Z^{\text{lin}} \approx 1/(1+\alpha/2) \) for all values of \( \alpha \), which tends to zero asymptotically. The D-M spectral function (without
numerical broadening) is

\[ A(x) = \frac{Z}{\omega_{LO}} \delta(x - x_{QP}) + \frac{1}{\pi \omega_{LO}} \frac{\alpha \sqrt{x - 1}}{x^2 (x - 1) + \alpha^2} \beta(x - 1), \]

where \( x = \omega/\omega_{LO} \) and \( x_{QP} = E_{QP}^{D}/\omega_{LO} \). The D-M side-band always starts at \( \omega = \omega_{LO} \), rather than at the intuitively correct value of \( E_{QP} + \omega_{LO} \). The Monte Carlo spectral functions\(^{22}\) show sidebands starting close to the intuitive energy.

VII. FULL MIGDAL SELF-ENERGY FROM FIRST-PRINCIPLES

We present now first-principles results for the full self energies (real and imaginary parts, from all phonon modes, including interband and Debye-Waller effects) of MgO and LiF, at the valence band maximum (VBM) and conduction band minimum (CBM). These results will be used in the next section to find D-M and cumulant spectral functions. This section also gives the related first-principles parameters to be fed into the Fröhlich model. For MgO and LiF band extrema, the Fröhlich coupling \( \alpha \) ranges from about 1.5 to 15. We also tabulate the magnitudes of the separate Debye-Waller and Fan terms, as well as their contributions from unoccupied and occupied states.

Technical details of the first-principles calculations are in the Appendix. The most delicate issue concerns the sampling of phonon wavevectors in the Brillouin zone, and the numerical broadening factor needed to treat Eq.(7). To obtain well-converged self energies, the eigenenergy differences between sampled wavevectors as well as the numerical broadening factor must be significantly smaller than the LO phonon frequency. This is especially important at the unperturbed quasiparticle eigenenergy, where the real and imaginary parts and their derivatives govern the asymptotics of the cumulant, and hence the quasiparticle peak characteristics. We choose a broadening of 0.01 eV, approximately \( \omega_{LO}/8 \) (see Table I), and wavevector grids up to \( 96 \times 96 \times 96 \) points for the CBM of MgO and \( 48 \times 48 \times 48 \) points for the other cases. This is considerably better than in Ref.\(^{58}\) for the same materials (diamond and BN were also studied in that work). Indeed, in Ref.\(^{58}\) the broadening factors ranged between 0.1eV and 0.4eV, and phonon wavevector grids had at most \( 32 \times 32 \times 32 \) points.

MgO and LiF both crystallize in the (cubic) rocksalt structure, with one formula unit per primitive cell. Density-Functional Theory (DFT-GGA) Kohn-Sham electronic structure of both materials can be found elsewhere\(^{86}\) and will not be reproduced here. In both materials, the CBM is not degenerate. It is parabolic in a large region around \( \Gamma \), so we expect the effective mass parabolic approximation to be adequate. The VBM is triply degenerate at \( \Gamma \). One light hole band rapidly separates from two heavy hole bands away from \( \Gamma \), the latter being degenerate along the \( \Gamma-X \) and \( \Gamma-L \) directions. The deviation with respect to parabolicity is faster than for the conduction band. The VBM eigenenergy is set to zero by convention. Concerning the phonon band structures, in both materials, there are three acoustic and three optical phonon branches. At \( \Gamma \), the LO branch is separated from the doubly-degenerate TO branches.

Table I presents the computed geometric, electronic, dielectric, and dynamical properties of MgO and LiF, that determine the corresponding Fröhlich parameter \( \alpha \), also reported in this table. The primitive cell parameter is \( a_0 = a/\sqrt{2} \), where \( a \) is the size of the conventional cube. Different effective masses are mentioned for the valence bands, corresponding to the heavy hole (hh) and to the light holes (lh), and also to different directions of the non-spherical electronic structure.\(^{85}\) Note that the dynamical properties of the two materials are rather similar, while their dielectric properties and effective masses differ significantly. The Fröhlich parameter \( \alpha \) provides a rough estimate of the phonon-induced zero-point renormalization of the quasiparticle energy. For the conduction band minimum, the estimated shifts (-\( \alpha \omega_{LO} \)) are -0.137eV for MgO and -0.332eV for LiF. For valence bands, we do not attempt to integrate over all effective mass directions and hole types, but simply provide the corresponding \( \alpha \) values deduced from Eq. (11). The values presented in Table I are in reasonable agreement with those recently computed in Ref.\(^{57}\) for the same materials. However, in the latter work, the Fröhlich polaron binding energy is defined as half the value from the usual theoretical approach (that we adopt), because the authors cut off the q-integral at \( \pi \) over the polaron radius instead of infinity. We find on the contrary that the Fröhlich values underestimate first-principles values, as will appear later.

| Table I. Computed basic characteristics of MgO and LiF. See text for the different symbols. |
|-----------------------------------------------|
| Unit | MgO | LiF |
| \( a_0 \) | \( \text{[Å]} \) | 3.01 | 2.88 |
| \( \Omega_0 \) | \( \text{[Å}^3 \) | 19.2 | 16.9 |
| \( \varepsilon_g \) (DFT-GGA) | \( \text{[eV]} \) | 4.49 | 8.54 |
| \( \omega_{LO}/\omega_{TO} \) | \( \text{[eV]} \) | 0.0844/0.0454 | 0.0828/0.0466 |
| \( \epsilon_{\infty}/\epsilon_0 \) | 3.23/11.14 | 2.04/6.44 |
| \( m^*_e \) | 0.340 | 0.873 |
| \( m_{hh}^* \) (Γ-X/Γ-L) | 2.164/3.822 | 3.622/11.955 |
| \( m_{lh}^* \) (Γ-X/Γ-L) | 0.387/0.335 | 1.346/0.887 |
| \( \alpha_{e} \) | 1.624 | 4.009 |
| \( \alpha_{hh} \) (Γ-X/Γ-L) | 4.101/5.450 | 8.165/14.834 |
| \( \alpha_{lh} \) (Γ-X/Γ-L) | 1.734/1.610 | 4.977/4.040 |

The self energy for the CBM of MgO, in a 2eV window around the bare electronic energy \( \epsilon_0 \), is presented in Fig. \( \[\] \). For sake of brevity, we introduce the notations \( \Sigma_1 = \Re \Sigma \) and \( \Sigma_2 = \Im \Sigma \). Fröhlich-type real and imaginary peaks, both negative, occur at \( \omega_{LO} \approx 0.0844 \text{eV} \), just as in Fig. \( \[\] \). Despite a very fine \( 96^3 \) q-point grid
FIG. 9. The MgO conduction band minimum retarded self energy with \( \delta = 0.01 \) eV and a 96\(^3\) \( q \)-grid. Full black line: imaginary part; dotted red line: real part. The reference energy \( \varepsilon^0 \) is the unrenormalized conduction band energy minimum. This figure agrees with Fig. 6, except that it includes all phonons and interband effects rather than just the analytic Fröhlich result.

sampling and a small 0.01 eV broadening of the denominators (see the Appendix), some numerical noise is still clearly visible. The Debye-Waller contribution, and the Fan contributions from bands other than lowest conduction, shift \( \Sigma_1 \) to more negative values compared to Fig. 6 and give it a slight linear slope in the vicinity of the conduction band minimum. This is shown in Fig. 10 that presents the same data in a wider energy window, also with the electronic density of states (DOS). Other structures are indeed present, in the valence band region (below \(-4\) eV), with the same van Hove singularities as the electronic DOS. Small structures in the conduction band region are seen as well.

Similarly, \( \Sigma_1 \) and \( \Sigma_2 \) for the VBM of MgO are shown in Fig. 11. With the same sampling and broadening as for the CBM, the noise can hardly be seen. Indeed, the curvature of the hole band is less pronounced for the VBM than for the CBM, making the numerical work less difficult. Close to \( \omega - \varepsilon^0 = 0 \), the structure of the self energy is close to the Fröhlich self energy, with the appropriate sign change for a hole polaron. Additional valence band characteristic features are seen, clearly related to the electronic DOS. By contrast, the imaginary part of the self energy in the conduction region is very small, and the real part is nearly structureless.

Unlike the electronic dispersion, the role of the phonon dispersion is apparently minor. Indeed, for the phonon frequencies to have an impact on the self energy, the difference between \( \omega \approx \varepsilon_{kn} \) and the electronic eigenenergies \( \varepsilon_{k+q0} \) must be comparable to phonon frequencies, see Eqs. 9 and 10. This happens only in a small Brillouin zone volume around \( \Gamma \), in which the phonon branches are practically constant.

The characteristics of the self energy, evaluated at the bare eigenenergy \( \varepsilon_{kn} \), are reported in Table II including the decomposition into Debye-Waller and Fan (and unoccupied/occupied) components. Also, the frequency derivative of the self energy and components are given. A 48 \( \times \) 48 \( q \)-wavevector grid has been used by default for this table, except for the real part of the self energies and their decomposition, which is also given using the more converged 96 \( \times \) 96 \( q \)-wavevector grid.

The convergence of the Allen-Heine-Cardona zero-point renormalization (ZPR) with respect to the wavevector sampling has been thoroughly analyzed in Sec. IV.B.2 of Ref. 57. In particular, for IR active materials treated in the non-adiabatic approximation, at the band structure extrema, a \( 1/N_q \) behavior is obtained,
TABLE II. MgO and LiF first-principles self energy (eV) and frequency derivative (dimensionless) at $\omega = \varepsilon_{\text{Kn}}$, and their components, for the conduction band minimum and valence band maximum. The Debye-Waller self energy is static (frequency-independent) and real. The quasiparticle weights, from linearized D-M and retarded cumulant approaches are also mentioned, as well as their occupied and unoccupied bands factors. For the real part of the self energy, results are reported with two different phonon wavevector grids ($96^3$ and $48^3$), while for the imaginary part, the derivatives and the quasi-particle weights, only the results obtained with the $48^3$ grid are reported.

|       | MgO CBM | MgO VBM | LiF CBM | LiF VBM |
|-------|---------|---------|---------|---------|
| $96^3$ grid |         |         |         |         |
| $\Sigma_1$ | -0.191 | 0.285 | -0.370 | 0.723 |
| $\Sigma_1^{\text{DW}}$ | -0.056 | 4.263 | 0.078 | 6.785 |
| $\Sigma_1^{\text{Fan},\text{un}}$ | -0.371 | -4.327 | -0.524 | -6.911 |
| $\Sigma_1^{\text{Fan},\text{oc}}$ | 0.235 | 0.349 | 0.077 | 0.850 |
| $48^3$ grid |         |         |         |         |
| $\Sigma_2$ | -0.175 | 0.285 | -0.342 | 0.695 |
| $\Sigma_1^{\text{DW}}$ | -0.054 | 4.263 | 0.078 | 6.772 |
| $\Sigma_1^{\text{Fan},\text{un}}$ | -0.354 | -4.327 | -0.497 | -6.898 |
| $\Sigma_1^{\text{Fan},\text{oc}}$ | 0.233 | 0.349 | 0.077 | 0.821 |

$\frac{\partial \Sigma_1}{\partial \omega}$ | -0.455 | -1.594 | -1.353 | -4.780 |
| $\frac{\partial \Sigma_1^{\text{Fan},\text{un}}}{\partial \omega}$ | -0.446 | -0.007 | -1.345 | -0.012 |
| $\frac{\partial \Sigma_1^{\text{Fan},\text{oc}}}{\partial \omega}$ | -0.009 | -1.587 | -0.008 | -4.768 |
| $\frac{\partial \Sigma_2}{\partial \omega}$ | -0.058 | -0.252 | -0.206 | -1.248 |
| $\frac{\partial \Sigma_2^{\text{Fan},\text{un}}}{\partial \omega}$ | -0.058 | 0.000 | -0.206 | 0.000 |
| $\frac{\partial \Sigma_2^{\text{Fan},\text{oc}}}{\partial \omega}$ | 0.000 | -0.252 | 0.000 | -1.248 |

$Z_{kn}^R$ = $Z_{kn}^b Z_{kn}^c$. (48)

Only one of these factors is included in the t-O cumulant weights of Refs. [9] [10] [22] and [17] (Eq. (3.64)), while both are present in Ref. [17] (Eq. (2.62)). In the former t-O approaches, the imaginary part of the self energy (which comes from the electron or hole-only self energy) is not consistent with the asymptotic limit of the cumulant, determined from the complete self energy expression, so that the spectral function is not normalized. However, as can be judged by the closeness to unity of $Z_{kn}^c$ in the VBM case and $Z_{kn}^h$ in the CBM case, in MgO and LiF, the normalization defect is very small: the smallest of these weights is at least 0.988, that is only 1.2% less than one. electronic gap and the largest phonon frequency.
Unlike $Z_R$, $Z^\text{Dlin}_n$ cannot be factorized in a product of occupied and unoccupied state contributions, see Eq. (15): $Z^\text{Dlin}_n$ and $Z_R$ spectral weights differ the most in the VBM case. For the LiF VBM case, the ratio exceeds one order of magnitude. It is slightly less than two for the MgO VBM. Taking into account the results from large polaron studies of the Fröhlich Hamiltonian (clearly favoring the Rayleigh or cumulant shifts, Eq. (11) and (29)), the values from Table I of Ref. 58, column $\Sigma^\text{dyn}_n(\omega_0)$ have also to be preferred over the values in columns $Z^\text{Dlin}_n(\omega_0)$ or $\Sigma^\text{dyn}_n(\epsilon)$. Similarly the values published in Ref. 57, Table VII, column “ZPR Non-adiabatic” correspond to the preferred expressions Eq. (11) and (29).

For completeness, Table II also mentions the imaginary values of the self energy and its derivative, respectively, linked physically to the broadening of the quasiparticle peak and its asymmetry. Note that these values are actually artificial effects of numerical broadening. Our computations only include band extrema at zero temperature, for which the imaginary part of Eqs. 9 and 10 vanish exactly if there is no artificial broadening. Nonzero values of $\Im \Sigma$ at the QP energy thus indicate the magnitude of the broadening parameter.

VIII. FIRST-PRINCIPLES SPECTRAL FUNCTIONS

Here we present the spectral functions of the CBM and VBM of MgO and LiF using $G_C$ and $G_D$, and examine their differences. The LiF VBM spectral function $A_{DM}$ from $G_D$ was previously given in Fig. 1 of Ref. 58, but our numerical treatment of $G_D$ is significantly improved.

We only use the retarded cumulant approach. It appears to be the preferred method to obtain the quasiparticle spectral functions for insulators as well as metals. The previous section has described, however, the similarity between retarded and time-ordered cumulants for our gapped materials, due to the smallness of the contribution of the occupied self energy to the CBM, and of the unoccupied self energy to the VBM.

Figs. 12 to 15 present D-M and retarded cumulant spectral functions, for the CBM and VBM of MgO and LiF, and also show the Fröhlich spectral function obtained with estimated $\alpha$ (Table II) for the CBM case. The phonon wavevector Brillouin zone has been sampled by a $96 \times 96 \times 96$ grid for the CBM of MgO, and a $48 \times 48 \times 48$ grid for the other cases. In all cases, a 0.01 eV $\approx 0.12\omega_{LO}$ broadening of the self energy has been used.

For the MgO CBM, with Fröhlich $\alpha = 1.62$, Fig 12 the position of the quasi-particle peak in the first-principles D-M case is lower than from the first-principles cumulant case. Moreover, the Fröhlich peak position is closer to the first-principles D-M position than with the first-principles cumulant one. This agreement between the D-M position and the Fröhlich peak position is accidental: the Fröhlich constant is too small to reproduce the band gap shift from first-principles (cf. the above mentined 50 – 70 meV underestimation), while the D-M shift is also too small, but this is due to the incorrect underestimation highlighted in Fig. 1. The position of the satellite follows the same pattern as observed for the Fröhlich Hamiltonian: the D-M satellite is separated from the quasiparticle peak by much more than the LO phonon frequency, while the distance between the satellite and the quasiparticle peak in the cumulant case is close to the LO phonon frequency value. Hence, we conclude that for the CBM of MgO, the spectral function shape is dominated by the LO phonon. First-principles and Fröhlich Hamiltonian approaches yield very similar shapes, although the Fröhlich approach underestimates the QP energy shift. This is an important result of the present work. The same conclusion will be obtained for the other band extrema, for both MgO and LiF.

In the LiF CBM case, with Fröhlich $\alpha = 4.01$ (Fig.13), the position of the quasi-particle peak in the D-M case is much higher than in the cumulant case. The Fröhlich-only cumulant peak position is close to the full-band cumulant one. Because the value of $\alpha$ is larger than for MgO, LiF has a larger second satellite before the smoothing of the spectral function. The same observations as for the MgO CBM, concerning the shape and position of the peaks, can also be made.

Despite the MgO valence band being three-fold degenerate at $\Gamma$, the MgO VBM case, Fig 14 is actually very similar to the LiF CBM case, with positive energy shifts seen instead of negative energy shifts.

Finally, in the case of LiF VBM, with the Fröhlich $\alpha$ being at most 14.8 for the heavy hole effective mass, Fig 15 the cumulant spectral function has become a broad peak (similar to Fig. 8) without any quasiparticle peak or satellite structure, unlike in the D-M case. The lack of structure in the cumulant spectral function results from the large value of the Fröhlich $\alpha$, directly linked to the large hole effective mass, i.e. the rather flat LiF valence bands.

IX. SUMMARY AND PERSPECTIVES

In this work, we compute from first principles the electron-phonon self energy for the electronic states at the band extrema of MgO and LiF, at zero temperature, from which we obtain the spectral function using both Dyson-Migdal and the cumulant methodologies. As decades of research on model systems emphasize the role of LO phonons in infrared-active semiconductors and insulators, we first provide an analysis of the self energy and spectral function of the Fröhlich Hamiltonian using the same methodologies.

For the imaginary part of the self energy, the characteristic inverse square root behavior of the Fan self energy found in the Fröhlich Hamiltonian, starting at the LO phonon frequency threshold, is also clearly present in MgO and LiF. However, additional structures, mirroring the electronic DOS are also present. They originate from
occupied as well as unoccupied bands, for both electron and hole self energies. By contrast, the role of the phonon dispersion is minor.

The real part of the Fröhlich Hamiltonian self energy has also an inverse square root behavior, on the other side of the LO phonon frequency threshold, compared to the imaginary part. This feature is also present in first-principles calculations, with additional structures mirroring the electronic DOS. The Debye-Waller self energy, that complements the Fan self energy, gives a global shift, impacting the zero-point renormalisation of eigenenergies.

To correctly obtain the inverse square root behavior in first-principles self energies, the numerical integration over the phonon wavevectors has to be done carefully, and its convergence monitored. Numerical broadening of the denominator present in the Fan self energy helps to reach convergence, but affects the accuracy of the prediction. Although schemes to overcome such convergence problems start to appear, we have simply performed the summation over a very fine grid, for a small broadening.

The real part of the electron-phonon self energy, evaluated at the bare eigenenergy, is directly linked to the shift of this bare eigenenergy, in the cumulant approach as well as in the simple Rayleigh-Schrödinger approach at lowest order. For the Fröhlich Hamiltonian, this correlates well with results from more sophisticated methods, for Fröhlich coupling constants up to about 10. An estimate of the corresponding Fröhlich coupling constant values for the conduction band minima gives about 1.62 for MgO and 4.01 for LiF, while for the valence band minima, the situation is more complex due to band degeneracy and warping, with values in the range 1.6 to 5.5 for MgO, and between 4.0 and 14.8 for LiF.

Our first-principles eigenenergy shifts range from 207 meV for the CBM of MgO to 751 meV for the VBM of LiF. Simple Fröhlich Hamiltonian estimates are too low although they account for a large fraction of such shift. However, detailed analysis shows that there is cancella-
tion between the Debye-Waller self energy (not taken into account in the Fröhlich Hamiltonian) and the Fan self energy. This cancellation is especially strong between the unoccupied part of the Fan self energy and the Debye-Waller self energy, in the case of the valence band minima for both MgO and LiF.

The derivative of the electron-phonon self energy with respect to the frequency, evaluated at the bare eigenenergy, is directly linked to the weight of the quasiparticle peak, in the cumulant approach. Different flavors of cumulant methodology are examined, based either on the retarded or t-O Green’s function. For these flavors, the inclusion of occupied and unoccupied band contributions to these weights differ in a rather simple way, e.g. the weight is a multiplicative function of the occupied and unoccupied contributions in the retarded Green’s function approach. Due to the large ratio between LO phonon frequency and energy gap, the predictions of the different cumulant approaches differ little (the normalisation weights differ by less than 2%). The difference might be larger for materials with smaller gaps and larger maximum phonon frequencies, as it will scale roughly as the ratio of these quantities.

We analyze detailed structure of spectral functions from both cumulant and Dyson-Migdal approaches, using both the Fröhlich Hamiltonian and full DFT. In the cumulant case, the separation between the quasiparticle peak and the first satellite corresponds to the LO phonon frequency. For equivalent Fröhlich coupling constant equal to about four, one also observes a second satellite, separated from the first one by the LO phonon frequency as well. Beyond these, the cumulant spectral function decays monotonically and any other structure is hard to discern, although this is impacted by the numerical (small) broadening that we have used. This behavior is very similar to that of the cumulant Fröhlich spectral function. For the LiF valence band maximum, the equivalent Fröhlich coupling constant is higher than four, and the spectral function is a broad peak, showing no quasiparticle peak. The behavior of the LiF and MgO spectral functions at valence and conduction band extrema in D-M theory differs strongly from that of the cumulant approach. In the former, there is always a clear quasiparticle peak, as well as a broad satellite feature, whose starting energy differs by more than the LO phonon frequency from the quasiparticle peak. This behavior is seen in the Fröhlich Hamiltonian case as well. Since the quasiparticle peak location is badly predicted from Dyson-Migdal theory even at low Fröhlich coupling constants, it is safe to argue that the shape of spectral function from the Dyson-Migdal approach can never be trusted.

Our conclusions should apply to a large class of infrared-active materials. In particular, the polar LO phonon contribution will give the biggest part of the zero-point renormalization and the spectral lineshape. It would be worth to examine more materials, and find a rule for when the Fröhlich Hamiltonian might give a reasonably accurate estimate of the electron-phonon quasiparticle shift. For the conduction band minimum, Fröhlich alone accounts for 4/5 of the CBM shift for LiF, but only 2/3 of the CBM shift for MgO. By contrast, the case of diamond is a remarkable example of a large QP shift without polar phonons. Its band edge zero-point renormalisation (−330 meV for the indirect gap, and −416 meV for the direct gap) has a magnitude similar to those of the infra-red active materials studied here.

Finally, angle-resolved photoemission (ARPES), although difficult in insulators, could provide a nice test of some of the predicted spectral functions in this paper. In particular, consider the MgO valence band maximum shown in Fig. 14. We predict a quasiparticle carrying 20% of the spectral weight, and clear phonon satellites. These may be accessible to experiment. However, by contrast, consider the valence band maximum of LiF, shown in Fig. 15. The prediction is a completely blurred quasiparticle (Z = 0.008), with a broad peak rather than distinct satellites. However, this prediction is outside the trust range of our approach. The α values for LiF are in the range 4 to 15, rather than 1.6 to 5.5 for MgO. Experiment shows that a hole at the top of the valence band of LiF self-traps in a local distortion similar to an F− ion. This trapped polaron is known as a V center. The present simple Hamiltonian (e.g. without anharmonicities) is insufficient to yield such a bound state. The perturbative spectral function correctly tells us that there is negligible weight in the quasiparticle peak. However, for holes at the top of the valence band in materials like LiF and NaCl, perturbation theory is not enough.

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APPENDIX. FIRST-PRINCIPLES CALCULATIONS: TECHNICAL DETAILS

All first-principles calculations are done using ABINITv8.4.1 (main executable abinit as well as post-processor ElectronPhononCoupling). The computations use density functional theory (DFT, ground state and
electronic structure) and density functional perturbation theory (DFT+phonons and electron-phonon coupling), as described in Refs. 78 and 79, with the PBE generalized gradient approximation (PBE-GGA) for MgO, and local density approximation (LDA) for LiF. See Ref. 93 for more information about the basic theories. The effective masses have been computed directly using the scheme from Ref. 93. The Allen-Heine-Cardona formalism is used for the computation of the Fan and Debye-Waller self energies,44,46,49,56 The summation over unoccupied bands is handled efficiently thanks to a reformulation in terms of a Sternheimer equation.57 However, in order to treat correctly the dynamical self energy, the contribution from a number of “active” bands is computed explicitly by a sum over states, as described in Ref. 57, see Eq. (15).

Atomic masses from natural isotopic ratio have been used throughout, namely (in atomic mass units), $M_{Mg} = 24.305$, $M_D = 15.9994$, $M_Li = 6.941$ and $M_F = 18.9984032$.

Norm-Conserving Pseudopotentials for MgO were taken from the ABINIT web site, generated using ONCVPSP, while for LiF Troullier-Martins pseudopotentials have been used. For both MgO and LiF, we used a $8^3$ Monkhorst-Pack grid sampling of the Brillouin Zone for the electronic wavefunctions, and a 50 Ha kinetic energy plane-wave cut-off. The summation over unoccupied bands for the dynamical self energy is made over 6 conduction bands for MgO, and 3 conduction bands for LiF, corresponding to a range of more than 10 eV above the CBM. The difference between the dynamical denominator (including the phonon frequency) and the static denominator (with only the electronic eigenenergy differences) is smaller than 1% above these bands, hence the summation over states can be safely replaced by the Sternheimer equation beyond them. Note that the replacement of an explicit sum over states, that includes a physical infinitesimal imaginary $\delta \eta$, by a static contribution from the Sternheimer equation destroys the Kramers-Kronig relations Eqs. 27 and 28. Of course, this has no influence on the real and imaginary parts directly computed in the low-energy region of the conduction bands or in the valence bands.

The phonon wavevector sampling that is needed to get converged self energies and spectral functions is a delicate issue, already mentioned in Ref. 58. The most difficult case is the CBM of MgO, since this band disperses quite strongly, as can be deduced from its low effective mass. In order to get the imaginary part of the self energy, the wavevector sampling ought to sample electronic eigenenergies such that their differences are not larger than the LO phonon frequency. This is hard to achieve when the effective mass is small. As described in Ref. 57, see in particular Eq. (16), a broadening factor $\delta$ is used to smooth the computed functions. Too large a $\delta$ value prevents distinguishing characteristic features of the self energy or spectral function, which may typically appear at scales of the LO phonon frequency.

Table III gives the effective masses of MgO and LiF, for the conduction band minima, for different wavevector samplings and broadening factors $\delta$.

![Fig. 16. Spectral function (Dyson-Migdal) of the MgO CBM self energy with a $20^3$ $q$-grid, and decreasing $\delta = 0.1$, 0.05, 0.02 eV. The separation between the quasiparticle peak and the satellite is still not complete with the smallest $\delta$ value.](image)

Table III. MgO self energy (eV) and frequency derivative (dimensional) at $\omega = \epsilon_{Q\alpha}$ for the conduction band minimum, for different wavevector samplings and broadening factors $\delta$.

| Wavevector grid | $\delta$ (eV) | $\Sigma$ | $\partial \Sigma / \partial \omega$ |
|-----------------|--------------|----------|----------------------------------|
| $20^3$          | 0.01         | -0.1391 - i 0.0008 | 0.0163 - i 0.0089 |
| $20^3$          | 0.02         | -0.1391 - i 0.0032 | -0.1589 - i 0.0177 |
| $20^3$          | 0.05         | -0.1381 - i 0.0078 | -0.1498 - i 0.0421 |
| $20^3$          | 0.10         | -0.1352 - i 0.0147 | -0.1232 - i 0.0712 |
| $20^3$          | 0.01         | -0.1391 - i 0.0016 | -0.1604 - i 0.0089 |
| $32^3$          | 0.01         | -0.1602 - i 0.0031 | -0.3086 - i 0.0294 |
| $48^3$          | 0.01         | -0.1746 - i 0.0050 | -0.4975 - i 0.0619 |
| $96^3$          | 0.01         | -0.1912 - i 0.0062 | -0.6264 - i 0.0968 |

Fig. 16 presents the D-M spectral function of the CBM of MgO with a $20^3$ $q$-grid, and $\delta$ values 0.1, 0.05 and 0.02 eV. Larger $\delta$ smoothes the function, but also modifies its shape: the clear and physical separation between the quasiparticle peak and the satellite is washed out.

The values of the self energy at the CBM are also strongly affected, as can be seen in Table III. From the numbers in this table, one can appreciate the convergence of the real part of the self energy as the inverse of $N_q$, mentioned in Sec. VII, mathematically derived in Ref. 57. This convergence study also highlights why the ZPR of the MgO CBM obtained in the present work, namely -207meV, is quite different from the same quantity presented in Table I of Ref. 58, namely -207meV, quite different from the same quantity presented in Table I of Ref. 58, $\Sigma^dm\omega(\epsilon_0)=-143$meV, although the same software and pseudopotentials have been used.

A 0.01 eV broadening appears maximum for a meaningful investigation of the different spectral functions and self energies. The self energy is even noier than the spectral function (see Fig. 17). Going from a $20^3$ sam-
FIG. 17. The imaginary part of the MgO CBM self energy with a $20^3$ q-grid and decreasing $\delta = 0.1, 0.05, 0.02 \text{ eV}$.

FIG. 18. The MgO CBM self energy with $\delta = 0.01 \text{ eV}$ and a $20^3$ q-grid. Full black line: imaginary part; dotted red line: real part.

The convergence parameters also impact the cumulant spectral functions, although they are more easily converged than the self energy or the D-M spectral function. The cumulant spectral functions corresponding to the VBM of MgO with $\delta = 0.01 \text{ eV}$ and $20^3$, $32^3$, $48^3$, and $64^3$ grids are presented in Fig. 19.

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