

## Unified Approach to Polarons and Phonon-Induced Band Structure Renormalization

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*Ab initio* calculations of the phonon-induced band structure renormalization are currently based on the perturbative Allen-Heine theory and its many-body generalizations. These approaches are unsuitable to describe materials where electrons form localized polarons. Here, we develop a self-consistent, many-body Green's function theory of band structure renormalization that incorporates localization and self-trapping. We show that the present approach reduces to the Allen-Heine theory in the weak-coupling limit, and to total energy calculations of self-trapped polarons in the strong-coupling limit. To demonstrate this methodology, we reproduce the path-integral results of Feynman and diagrammatic Monte Carlo calculations for the Fröhlich model at all couplings, and we calculate the zero point renormalization of the band gap of an ionic insulator including polaronic effects.

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The past decade has seen much progress in first-principles calculations of phonon-induced renormalization of band structures, including temperature dependence and quantum zero-point effects [1,2]. For example, since the initial *ab initio* implementations [3,4] of the Allen and Heine (AH) theory [5], several improvements have been made, including calculations of complete band structures of semiconductors [6–9] and nonadiabatic effects [10,11]. On a related front, *ab initio* many-body Green's function approaches have been used to calculate [12–22] band structure kinks and satellites observed in angle resolved photoelectron spectra [23–29], cf. Figs. 1(a) and 1(b). One important limitation of these methods is that they do not consider the possibility of electron localization into a polaron.

A polaron forms when an excess electron induces a distortion of the crystal lattice, which in turn acts as a potential well and promotes electron localization [30–32]. Calculations of polarons are usually performed by adding or removing an electron from a large supercell using density-functional theory (DFT) [33–39], cf. Figs. 1(d) and 1(e). To overcome the DFT self-interaction error and the computational complexity of large supercell calculations, this direct approach has recently been reformulated as a nonlinear eigenvalue problem within density-functional perturbation theory (DFPT) [40,41]. These “polaronic” methods carry two limitations: ions are described using the adiabatic Born-Oppenheimer approximation, and quantum nuclear effects are neglected.

The relation between AH-based approaches, which include many-body effects but do not consider electron localization, and polaronic approaches, which capture localization effects but do not include nonadiabaticity and quantum fluctuations, remains unclear. In particular, it is unclear whether these methods describe the same physics, so that they can be used interchangeably, or else they capture separate phenomena. Furthermore, it is unclear whether one approach is to be preferred over another for specific classes of materials.

Here, we address these questions by developing a self-consistent many-body Green's function theory of phonon-induced band structure renormalization that includes non-adiabatic effects and localization on the same footing. We show that the present theory reduces to AH-based approaches for materials that host large polarons, and to the *ab initio* polaron equations of Ref. [41] for materials with small polarons. To illustrate the broad applicability of this method, we calculate the energy of the Fröhlich polaron, and we obtain very good agreement with the path integral results of Feynman [42] and with diagrammatic Monte Carlo calculations [43,44]. As a first *ab initio* calculation using this method, we obtain the phonon-induced band gap renormalization of LiF, and we show that polaron localization effects dominate over the standard Fan-Migdal (FM) and Debye-Waller (DW) self-energies [2].

The effective Hamiltonian describing a coupled electron-phonon system is given by [2,45]

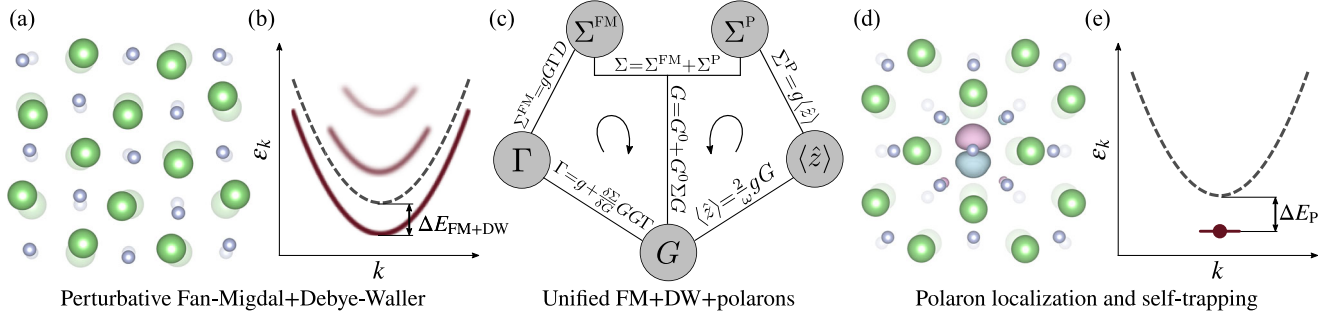


FIG. 1. (a) Schematic illustration of the ground state of the  $N$ -electron system, with atoms vibrating around the equilibrium sites of the periodic crystal. (b) Schematic of phonon-induced band structure renormalization, as obtained by using the FM and DW self-energies. The dashed line is the noninteracting band, the brown lines are the renormalized band and its phonon sidebands. (c) Self-consistent set of equations for calculating electron-phonon renormalization of band structures including polaron localization effects, Eqs. (1)–(4). (d) Schematic illustration of the ground state of the  $N + 1$ -electron system, where the excess electron forms a localized polaron. (e) In the scenario illustrated in (d), the energy of the conduction band bottom is lowered by the formation energy of the polaron.

$$\hat{H} = \sum_{n\mathbf{k}} \varepsilon_{n\mathbf{k}} \hat{c}_{n\mathbf{k}}^\dagger \hat{c}_{n\mathbf{k}} + \sum_{\mathbf{q}\nu} \hbar\omega_{\mathbf{q}\nu} (\hat{a}_{\mathbf{q}\nu}^\dagger \hat{a}_{\mathbf{q}\nu} + 1/2) + N_p^{-1/2} \sum_{\substack{\mathbf{k}, \mathbf{q} \\ mn\nu}} g_{mn\nu}(\mathbf{k}, \mathbf{q}) \hat{c}_{m\mathbf{k}+\mathbf{q}}^\dagger \hat{c}_{n\mathbf{k}} (\hat{a}_{\mathbf{q}\nu} + \hat{a}_{-\mathbf{q}\nu}^\dagger), \quad (1)$$

where  $\varepsilon_{n\mathbf{k}}$  represents the single-particle eigenvalue of an electron in the band  $n$  with crystal momentum  $\mathbf{k}$ ,  $\omega_{\mathbf{q}\nu}$  is the frequency of a phonon in the branch  $\nu$  with crystal momentum  $\mathbf{q}$ , and  $\hat{c}_{n\mathbf{k}}^\dagger/\hat{c}_{n\mathbf{k}}$  and  $\hat{a}_{\mathbf{q}\nu}^\dagger/\hat{a}_{\mathbf{q}\nu}$  are the associated fermionic and bosonic creation and annihilation operators, respectively;  $g_{mn\nu}(\mathbf{k}, \mathbf{q})$  denotes the electron-phonon coupling matrix element between the electrons  $n\mathbf{k}$  and  $m\mathbf{k} + \mathbf{q}$  via the phonon  $\mathbf{q}\nu$ , and  $N_p$  is the number of unit cells in the periodic Born-von Kármán supercell. The limitations of the effective Hamiltonian in Eq. (1) are discussed in the companion manuscript [45]

To investigate the ground state of the Hamiltonian in Eq. (1) in the presence of an excess electron or hole, we focus on the electron Green's function. We consider a periodic crystal with  $N$  electrons, and we define the electron Green's function as the expectation value of the field operators over the ground state of the  $N + 1$ -particle system:  $G_{12} = -(i/\hbar)\langle N + 1 | \hat{T} \hat{c}_1 \hat{c}_2^\dagger | N + 1 \rangle$ . In this definition we use the compact notation  $1 = \{n_1, \mathbf{k}_1, t_1\}$  and  $2 = \{n_2, \mathbf{k}_2, t_2\}$ ,  $t$  is the time, and  $\hat{T}$  is the time-ordering operator. Our present definition of Green's function differs from the conventional definition [46] where the expectation value is over the ground state  $|N\rangle$ ; this choice is essential to capture localization effects. Using Schwinger's functional derivative technique [2,46,47], in the companion manuscript [45] we derive the following Dyson equation:

$$G_{12} = G_{12}^0 + G_{13}^0 (\Sigma_{34}^{\text{FM}} + \Sigma_{34}^P) G_{42}, \quad (2)$$

where summation over repeated numbered indices is implied throughout the manuscript. In this expression,

$G^0$  is the Green's function in the absence of electron-phonon interactions,  $\Sigma^{\text{FM}}$  is the Fan-Migdal self-energy [2,48–50], and  $\Sigma^P$  is a new contribution that we call “polaronic” ( $P$ ) self-energy.

The Fan-Migdal self-energy is given by:

$$\Sigma_{12}^{\text{FM}} = ig_{314} G_{3(1),5} \Gamma_{526} D_{6,4(1)}, \quad (3)$$

where the electron-phonon matrix elements is written compactly as  $g_{123} = N_p^{-1/2} g_{n_2 n_1 \nu_3}(\mathbf{k}_1, \mathbf{q}_3) \delta_{\mathbf{k}_2, \mathbf{k}_1 + \mathbf{q}_3}$ , the notation  $G_{3(1),5}$  stands for  $G_{n_3 \mathbf{k}_3, n_5 \mathbf{k}_5}(t_1, t_5)$ , and there is no summation over bracketed indices. In Eq. (3),  $D$  is the phonon Green's function and  $\Gamma$  is the electron-phonon vertex; explicit expressions for these quantities are provided in Ref. [45].

The polaronic self-energy  $\Sigma^P$  appearing in Eq. (2) is given by

$$\Sigma_{12}^P = \delta(t_1 - t_2) g_{213} \frac{\langle \hat{z}_3 \rangle}{l_3}. \quad (4)$$

In this equation,  $l_3 = l_{\mathbf{q}\nu}$  is a short for the zero-point displacement amplitude, and the term  $\langle \hat{z}_3 \rangle = \langle \hat{z}_{\mathbf{q}\nu} \rangle$  represents the expectation value of the normal vibrational coordinates  $\hat{z}_{\mathbf{q}\nu}$  over the ground state of the  $N + 1$ -particle system,  $\langle N + 1 | \hat{z}_{\mathbf{q}\nu} | N + 1 \rangle$ , which is directly related to the atomic displacements in the polaronic configuration [45]. This expectation value depends in turn on the many-body electron density via the equal-time Green's function,  $\langle \hat{z}_3 \rangle = -il_3(2/\omega_3) g_{453}^* G_{5(1),4(1^+)}$  [45].  $\Sigma^P$  is nonzero whenever the atoms of the  $N + 1$ -electron ground state are displaced from the equilibrium sites of the  $N$ -electron ground state; hence, it describes polaron localization effects.

Equations (1)–(4) define a self-consistent formulation of the electron-phonon renormalization of energy bands that includes the effects of polaron formation. The relation

between these equations is schematically illustrated in Fig. 1(c).

Since our formalism starts from Eq. (1), which does not include terms of second order in the atomic displacements, our self-energy  $\Sigma$  does not contain the standard Debye-Waller contribution. This term must be added separately, as described in the companion manuscript [45].

The above formalism can be turned into a practical computational method by expressing the Fourier transform of the Green's function into frequency domain  $\omega$  via Dyson orbitals  $f_s(\mathbf{r})$  using the Lehmann representation,  $G(\omega) = \sum_s f_s f_s^* / [\hbar\omega - \varepsilon_s - i\eta \text{sgn}(\mu - \varepsilon_s)]$ , where  $\mu$  is the chemical potential, and  $\eta \rightarrow 0^+$ . The Dyson orbitals of the occupied manifold are given by  $f_s(\mathbf{r}) = \langle N, s | \hat{\psi}(\mathbf{r}) | N+1 \rangle$  [45,46], where  $|N, s\rangle$  denotes the  $s$ th excited state of the  $N$ -electron system,  $\hat{\psi}(\mathbf{r})$  is the electron field operator, and  $\varepsilon_s = E_{N+1} - E_{N,s}$ . In Ref. [45] we show that we can identify the Dyson orbital for the lowest-energy excitation of the  $N+1$ -particle system with the electronic component of the polaron wave function. Following the strategy of Ref. [41], we expand the orbitals in the basis of single-particle Bloch wave functions  $\psi_{n\mathbf{k}}$ ,  $f_s = N_p^{-1/2} \sum_{n\mathbf{k}} A_{n\mathbf{k}}^s \psi_{n\mathbf{k}}$ . This representation allows us to recast Eqs. (2)–(4) into a nonlinear eigenvalue problem for the quasiparticle amplitudes  $A_{n\mathbf{k}}^s$  and the electron addition or removal energies  $\varepsilon_s$ :

$$[\varepsilon_1 \delta_{12} + \Sigma_{12}^{\text{FM}}(\varepsilon_s/\hbar) + \Sigma_{12}^{\text{P}}] A_2^s = \varepsilon_s A_1^s, \quad (5)$$

where

$$\Sigma_{12}^{\text{FM}}(\omega) = \pm g_{143}^* g_{253} \sum_s \frac{A_4^s A_5^{s*}}{N_p} \frac{\theta[\pm(\varepsilon_s - \mu)]}{\pm \hbar\omega \mp \varepsilon_s - \hbar\omega_3 + i\eta}, \quad (6)$$

$$\Sigma_{12}^{\text{P}} = -\frac{2g_{213}g_{543}^*}{\hbar\omega_3} \sum_s^{\varepsilon_s < \mu} \frac{A_4^s A_5^{s*}}{N_p}. \quad (7)$$

In Eq. (6), there is a sum over the  $\pm$  terms and  $\theta$  is the Heaviside step function. The same expressions are given without using compact notation in Eqs. (41) and (45) of the companion manuscript [45]. To reach Eq. (6) we approximated the vertex  $\Gamma$  by the standard electron-phonon matrix element  $g$ , and we replaced the interacting phonon Green's function  $D$  by its adiabatic counterpart, as obtained, e.g., from DFPT calculations.

Equations (5)–(6) are still too complex for *ab initio* calculations. To proceed further, we assume that the added electron in the  $(N+1)$ -electron system has a negligible effect on the valence manifold of the  $N$ -electron system. The validity of this assumption is assessed in Ref. [45]. With this choice, the  $N$  occupied Dyson orbitals can be replaced by Bloch wave functions, and their contribution to  $\Sigma^{\text{P}}$  vanishes, while the Dyson orbital of the excess electron is to be determined by solving the equations self-consistently. After this simplification, and replacing the

Green's function by its noninteracting counterpart in Eq. (6), where Eqs. (6) and (7) become

$$\Sigma_{n\mathbf{k},n'\mathbf{k}'}^{\text{FM}}(\omega) = \pm \frac{\delta_{n\mathbf{k},n'\mathbf{k}'}}{N_p} \sum_{mq\nu} |g_{mq\nu}(\mathbf{k}, \mathbf{q})|^2 \times \frac{\theta[\pm(\varepsilon_{m\mathbf{k}+\mathbf{q}} - \mu)]}{\pm \hbar\omega \mp \varepsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{q\nu} + i\eta}, \quad (8)$$

$$\Sigma_{n\mathbf{k},n'\mathbf{k}'}^{\text{P}} = -\frac{2}{N_p^2} \sum_{mm'\nu\mathbf{k}''} A_{m'\mathbf{k}''+\mathbf{k}-\mathbf{k}'} A_{m\mathbf{k}}^* \times \frac{g_{m'\nu}^*(\mathbf{k}'', \mathbf{k}-\mathbf{k}') g_{m\nu}(\mathbf{k}', \mathbf{k}-\mathbf{k}')}{\hbar\omega_{\mathbf{k}-\mathbf{k}'\nu}}. \quad (9)$$

These equations can be solved by using electron band structures, phonon dispersions, and electron-phonon matrix elements from DFT and DFPT, as we show below. Once obtained the Dyson orbital and quasiparticle eigenvalue by solving Eqs. (5), (8), and (9), we determine the ground-state energy of the  $(N+1)$ -electron system using a generalized Galitskii-Migdal formula [51] that we derived in Ref. [45] for the coupled electron-phonon Hamiltonian in Eq. (1).

The Fan-Migdal self-energy in Eq. (8) is diagonal in the electron wave vector; therefore, this term does not contribute to electron localization. Thus, the shape of the polaron quasiparticle is determined by the polaronic term, and in the lowest-order approximation we can evaluate Eqs. (8) and (9) using a simplified procedure where we first solve for the polaron wave function with Eq. (9), and then we include  $\Sigma^{\text{FM}}$  using perturbation theory. In Ref. [45] we show that this procedure leads to the following expression for the polaronic total energy renormalization of the system with an excess electron:

$$\Delta E = N_p^{-1} \sum_{n\mathbf{k}} |A_{n\mathbf{k}}|^2 [\varepsilon_{n\mathbf{k}}^0 - \varepsilon_{\text{CBM}}^0 + \Sigma_{n\mathbf{k},n\mathbf{k}}^{\text{FM}}(\omega = \varepsilon_{\text{CBM}}^0/\hbar)] + \frac{1}{2} N_p^{-1} \sum_{n\mathbf{k},n'\mathbf{k}'} A_{n\mathbf{k}}^* \Sigma_{n\mathbf{k},n'\mathbf{k}'}^{\text{P}} A_{n'\mathbf{k}'}, \quad (10)$$

where  $\varepsilon_{\text{CBM}}^0$  represents the energy of the conduction band minimum of the periodic, undistorted lattice. This expression has an appealing physical interpretation. The first term on the right-hand side is the weighted average of the conduction band energy and the Fan-Migdal self-energy, taken over the polaron wave function coefficients in reciprocal space. The last term is the stabilization energy of the electron wave function resulting from the lattice distortion in the polaronic ground state. Therefore, the total energy renormalization is a combination of both AH-type and polaronic contributions, with their relative importance being dictated by the spatial extent of the wave function. To illustrate this point, we apply the present methodology to the Fröhlich model [31,52–54].

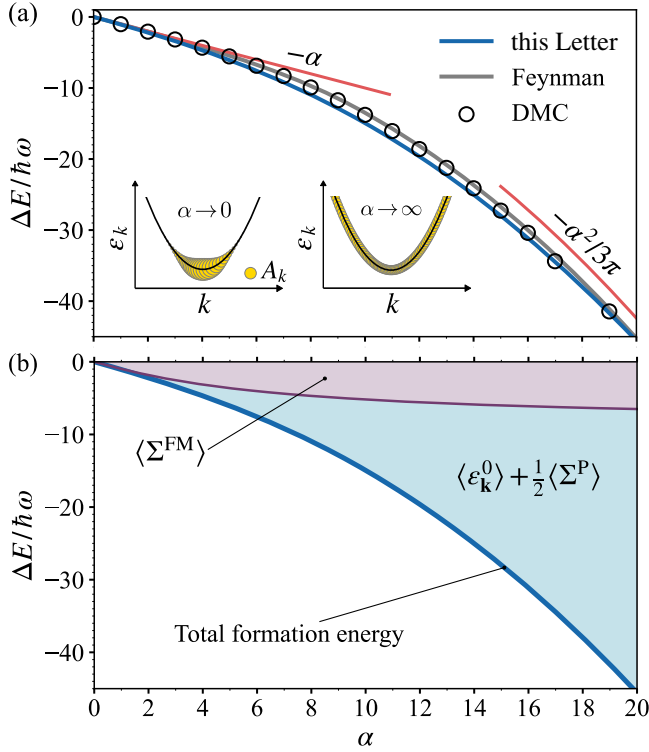


FIG. 2. (a) Ground-state energy of the Fröhlich polaron,  $\Delta E/\hbar\omega$ , as a function of the coupling strength  $\alpha$ : present calculation (blue line), Feynman's path integral results [42] (gray line), and diagrammatic Monte Carlo (DMC) data taken from Ref. [58] (black circles). Red lines indicate the asymptotic expansions at weak and strong coupling, respectively. The quasiparticle amplitudes  $|A_k|^2$  in these limits are shown in the inset, superimposed to the free electron band. (b) Breakdown of the ground-state energy of the Fröhlich polaron into its self-energy contributions.

The Fröhlich model is a standard benchmark for testing theories of coupled electrons and phonons [31]. It describes a free electron coupled to a dispersionless longitudinal optical phonon, with the coupling strength controlled by a dimensionless parameter, the Fröhlich coupling constant  $\alpha$ . AH-based approaches are successful in describing the weak-coupling regime ( $\alpha \ll 1$ ) of this model, while polaronic approaches such as the Landau-Pekar theory [55,56] are successful at strong coupling ( $\alpha \gg 10$ ) [57], cf. Fig. 2(a). State-of-the-art numerical results for the ground-state energy of the Fröhlich polaron come from diagrammatic Monte Carlo methods [43,44,58]. As of today, the only theory that matches diagrammatic Monte Carlo results at all coupling strengths is the variational path integral approach by Feynman [42,59].

Figure 2(a) shows the energy of the Fröhlich polaron as a function of  $\alpha$ , as calculated from Eq. (10). The agreement between our present approach and both Feynman's solution and diagrammatic Monte Carlo data is very good at all couplings. In particular, our method correctly captures the expected linear dependence of the energy on  $\alpha$  at weak

coupling,  $\Delta E = -\alpha\hbar\omega$ , and its quadratic dependence at strong coupling,  $\Delta E = -\alpha^2\hbar\omega/3\pi$  [31], cf. Fig. 2(a). These limits can be rationalized by examining the relative contributions to the total energy shown in Fig. 2(b). At small  $\alpha$ , the quasiparticle amplitudes concentrate near the conduction band bottom (CBM), thus leading to large polarons in real space [cf. inset of Fig. 2(a)]. In this limit, the expectation value of  $\Sigma^P$  tends to vanish, and the Fan-Migdal self-energy tends to  $\Sigma^{\text{FM}} = -\alpha\hbar\omega$ . Conversely, at large  $\alpha$  the quasiparticle amplitudes spread across the entire reciprocal space, leading to electron localization into a small polaron. In this limit,  $\Sigma^P = -\alpha^2\hbar\omega/3\pi$  dominates.

To illustrate the use of the present method for real materials, we calculate the zero-point renormalization of rock salt LiF, a prototypical ionic insulator. This system hosts both large electron polarons and small hole polarons [41]; therefore, it is particularly suited to analyze the relative magnitude of the various self-energies in the valence and conduction bands. All calculations are based on QUANTUM ESPRESSO [60], WANNIER90 [61], and EPW [62], and the computational setup is described in the companion manuscript [45]. We initialize the self-consistent solution of the polaron equations with a Gaussian wave packet. This step is needed to break translational symmetry, as discussed in Ref. [45]. We verified that different initializations lead to equivalent self-consistent polaron solutions in all cases [45].

Figure 3 summarizes our results. In panels (a) and (b) we show the renormalization of the conduction band minimum and of the valence band maximum with respect to the DFT band edges, respectively. The quasiparticle amplitudes are represented by the solid yellow circles superimposed to the bands, with the radius being proportional to the square modulus  $|A_{nk}|^2$ . In panels (c) and (d) we show how the AH band shift varies along the conduction and valence bands, respectively. In these calculations we evaluate the correction by including both the Fan-Migdal and the Debye-Waller self-energies,  $\Sigma^{\text{FM}} + \Sigma^{\text{DW}}$  [45], to be consistent with previous work [18]. In both cases we see that this correction is largest at the zone center, and decreases toward the edges of the Brillouin zone. The localization of the polaron wave function softens this correction by averaging it over a range of wave vectors, according to the quasiparticle amplitudes shown in (a) and (b).

In panels (e) and (g) of Fig. 3 we compare standard calculations of band renormalization using the Fan-Migdal and Debye-Waller self-energies (FM and DW) with our present approach. In the conduction band, the FM and DW corrections (0.43 eV) are seen to yield a similar result as the total polaronic renormalization (0.60 eV). This finding is consistent with the observation that an excess electron in LiF forms a large electron polaron extended over more than 10 unit cells, as shown in panel (d). In this scenario, the electron wave function is so delocalized that AH-based approaches provide a good description of the energy

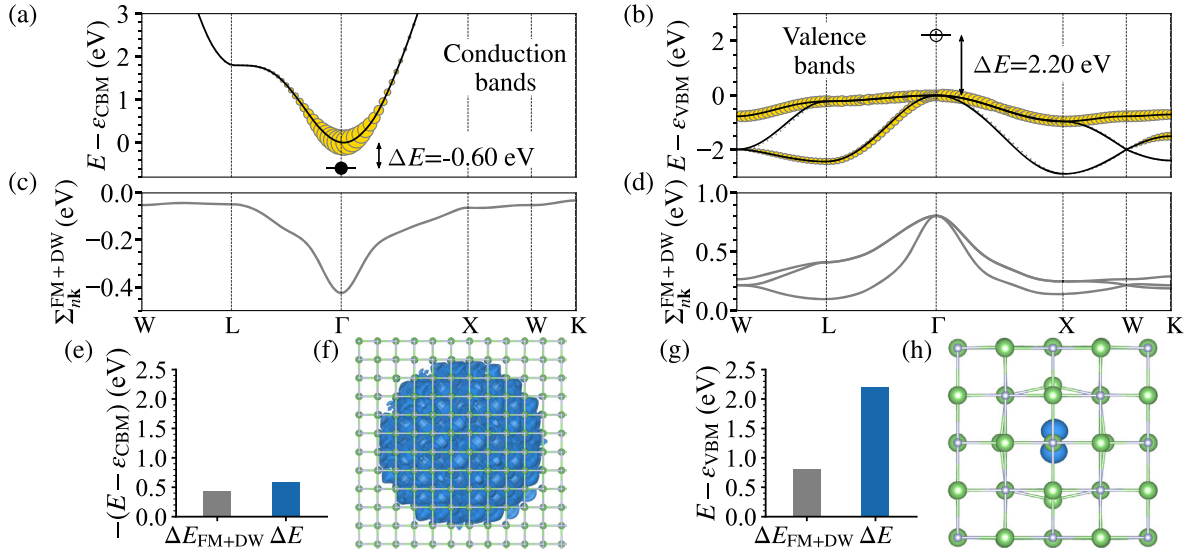


FIG. 3. (a), (b) Conduction and valence bands of LiF, with energies referred to the conduction band minimum (CBM) and to the valence band maximum, respectively. The yellow disks indicate the square moduli of the quasiparticle amplitudes of the Dyson orbitals, as obtained by solving Eqs. (5), (8), and (9). In each panel we indicate the quasiparticle renormalization including polaronic effects,  $\Delta E$ . (c), (d) Expectation values of  $\Sigma^{\text{FM}} + \Sigma^{\text{DW}}$  along the bands. (e), (g) Calculated renormalization of the conduction and valence band extrema, respectively, using two methods: the standard perturbative approach that does not include polaron localization (gray), and the present approach including localization effects (blue). (f), (h) Calculated wave functions of the electron and hole polarons in LiF, respectively.

renormalization. Conversely, in the valence bands the polaronic renormalization (2.20 eV) is much larger than the FM and DW corrections (0.80 eV). This finding is consistent with the fact that an excess hole in LiF forms a small polaron, as shown in panel (h).

By combining the above zero-point corrections for the valence and conduction band edges, we obtain a quantum zero-point quasiparticle band gap renormalization of  $-2.8$  eV. This value is considerably larger than what one obtains by using the Fan-Migdal and Debye-Waller self-energies at the band edges,  $-1.2$  eV. This difference suggests that AH-based approaches may not be as reliable as previously thought in calculations of band gap renormalization, because they do not take into account localization effects. We emphasize that this conclusion holds for systems that host spatially localized polaronic states such as ionic compounds and oxides. Standard semiconductors such as silicon and diamond [3,4,6,7,11] do not host localized polarons; therefore, in such cases AH-based approaches remain the current state of the art.

In summary, we developed a self-consistent many-body theory of electron-phonon couplings that unifies calculations of phonon-induced energy band renormalization and polaron localization. We found that the lowest-order approximation to our theory matches Feynman's results for the Fröhlich polaron. This methodology is amenable to first-principles implementations, as we have demonstrated for LiF. Future work will need to systematically assess polaronic corrections to the band renormalization of

semiconductors and insulators, investigate the present formalism beyond the lowest-order approximation, and extend this work to calculations of complete band structures, phonons sidebands in angle-resolved photoemission spectroscopy spectra, finite-temperature effects, and optical band gaps including excitonic effects. We hope that this study will stimulate renewed efforts to understand polarons and their properties in real materials.

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