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Phonon Screening of Excitons in Semiconductors: Halide Perovskites and Beyond

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The *ab initio* Bethe-Salpeter equation (BSE) approach, an established method for the study of excitons in materials, is typically solved in a limit where only static screening from electrons is captured. Here, we generalize this framework to also include dynamical screening from phonons at lowest order in the electron-phonon interaction. We apply this generalized BSE approach to a series of inorganic lead halide perovskites, CsPbX_3 , with $\text{X} = \text{Cl}, \text{Br}, \text{and I}$. We find that inclusion of screening from phonons significantly reduces the computed exciton binding energies of these systems. By deriving a simple expression for phonon screening effects, we reveal general trends for the importance of phonon screening effects in semiconductors and insulators, based on a hydrogenic exciton model. We demonstrate that the magnitude of the phonon screening correction in isotropic materials can be reliably predicted using four material specific parameters: the reduced effective mass, the static and optical dielectric constants, and the phonon frequency of the most strongly coupled LO phonon mode. This framework helps to elucidate the importance of phonon screening and its relation to excitonic properties in a broad class of semiconductors.

Excitons are central to a wide range of optoelectronic applications, from photovoltaics and photocatalysis, to light emission and lasing [1–4]; they emerge from the many-body interactions between charge carriers, photons, and phonons in optoelectronic materials [5]. In many bulk semiconductors, weakly bound Wannier-Mott excitons can be understood with a hydrogenic model [6, 7], in which the attractive Coulomb interaction between a photoexcited electron-hole pair is screened by a dielectric constant ϵ . In this picture, the exciton binding energy is $\mu/(2\epsilon^2)$ in atomic units, where μ is the magnitude of the reduced effective mass of the electron-hole pair [6]. Optical measurements under high magnetic fields use this model to extract the exciton binding energy, E_B and μ [8, 9]. In ionic or multicomponent semiconductors, an “effective dielectric constant”, $\epsilon_{\text{eff}} = \sqrt{2E_B/\mu}$, is frequently reported, usually taking values between the optical, ϵ_∞ , and static, ϵ_0 , dielectric constants. The use of ϵ_{eff} approximately accounts for the fact that the electron-hole interaction is screened by both the electrons and phonons [2, 10, 11]. However, it also obscures the details of specific phonons contributing to ϵ_{eff} , and it does not explain whether or why electron or phonon screening might be important in a given case. Rigorous *ab initio* calculations would therefore be of great value in this context.

Ab initio many-body perturbation theory calculations within the *GW* approximation [12, 13] and the Bethe-Salpeter equation (BSE) [14, 15] approach have been successful in quantitatively understanding the quasiparticle band structure and optical excitations of materials ranging from the simplest III-V semiconductors [16] to materials with heavy elements [17] or hybrid organic-inorganic components [18], low dimensionality [19], and intrinsic defects [20]. First principles methods including the effects of lattice vibrations have led to new understanding of the renormalization of the electronic band structure due to electron-phonon interactions [21–23],

as well as optical absorption [24, 25] and photoluminescence lineshapes [26, 27].

Recently, several first principles studies of a broad range of materials predicted exciton binding energies which are overestimated with respect to experiment [28–33]. In particular, Ref. [32] recently reported calculated exciton binding energies of hybrid organic-inorganic lead-halide perovskites which overestimate experimental measurements by up to a factor of 3. Ref. [32] attributed this overestimation to the coupling of the constituent free electrons and holes to phonons (hereafter referred to as ‘polaronic effects’). On the other hand, Ref. [33] used an approximate model dielectric function to conclude that phonon screening due to infrared active phonons renormalizes the exciton binding energy by up to 50%, bringing calculated values in much closer agreement with experiment. Since both reports are based on approximate hypotheses and implementations of phonon effects, it is not yet clear how these conclusions may be reconciled, in the absence of a complete *ab initio* calculation. The problem of electrons and holes interacting in a phonon field has been studied using phenomenological models, assuming parabolic electronic band structure and a phonon spectrum consisting of a single dispersionless phonon [10, 11, 34–36]. However, rigorous inclusion of polaronic and phonon screening effects within the BSE formalism remains an open challenge.

In this Letter, we extend the standard *ab initio* BSE formalism to include phonon screening effects at lowest order in the electron-phonon interaction. We introduce an additive, $\mathbf{q}$ - and ω -dependent contribution to the screened Coulomb interaction, W , associated with phonons, adopting a general form developed by Hedin and Lundquist [37] but neglected in contemporary calculations. We apply this framework to a set of all-inorganic lead-halide perovskite crystals in the low temperature, orthorhombic phase using the *ab initio* Fröhlich electron-phonon vertex introduced in Ref. [38], and we show

that phonon screening plays a major, but not exclusive, role in the exciton binding energies of this emergent class of optoelectronic materials. Finally, we develop a simple but general expression for the phonon-screened exciton binding energy for arbitrary isotropic semiconductors in terms of μ , ε_∞ , ε_0 , and ω_{LO} , providing a means for identifying semiconductors for which phonon screening effects will be significant.

In the standard *ab initio* reciprocal-space *GW*-BSE approach, the BSE can be written, in the Tamm-Dancoff approximation [14, 16], as

$$\Delta_{c\mathbf{k}v\mathbf{k}} A_{c\mathbf{k}}^S + \sum_{c'\mathbf{v}'\mathbf{k}'} K_{c\mathbf{k},c'\mathbf{v}'\mathbf{k}'}(\Omega_S) A_{c'\mathbf{v}'\mathbf{k}'}^S = \Omega_S A_{c\mathbf{k}}^S, \quad (1)$$

where $\Delta_{c\mathbf{k}v\mathbf{k}} = E_{c\mathbf{k}} - E_{v\mathbf{k}}$, with $E_{c\mathbf{k}}$ and $E_{v\mathbf{k}}$ the quasiparticle energies of the free electron and hole with band indices and wavevectors $c\mathbf{k}$ and $v\mathbf{k}$, respectively, usually calculated within the *GW* approximation [12, 13]. Exciton energies and expansion coefficients, in the electron-hole basis, are given by Ω_S , and $A_{c\mathbf{k}}^S = \langle c\mathbf{k}|S \rangle$ respectively, with S the principal quantum number for the exciton, and $|c\mathbf{k}\mathbf{v}\mathbf{k}\rangle$ the product state of an electron-hole pair, where the components of the products are typically Kohn-Sham wave functions computed with density functional theory (DFT) [41].

The electron-hole kernel, K , couples products of the single-particle states and is, at lowest order, written as the sum of two terms, a repulsive exchange term, $K^\times$, which is negligible for weakly bound excitons [42], and an attractive direct term, K^D , given by, as in Ref. [42],

$$K_{c\mathbf{k},c'\mathbf{v}'\mathbf{k}'}^D(\Omega) = - \left\langle c\mathbf{k} \left| \frac{i}{2\pi} \int d\omega e^{-i\omega\eta} W(\mathbf{r}, \mathbf{r}'; \omega) \times \left[\frac{1}{\Omega - \omega - \Delta_{c'\mathbf{k}'v\mathbf{k}} + i\eta} + \frac{1}{\Omega + \omega - \Delta_{c\mathbf{k}v'\mathbf{k}'} + i\eta} \right] \right| c'\mathbf{v}'\mathbf{k}' \right\rangle, \quad (2)$$

where η is a positive infinitesimal quantity, and $W(\mathbf{r}, \mathbf{r}'; \omega)$ is the time-ordered screened Coulomb interaction, which typically only includes electronic contributions to screening. In general, the BSE must be solved self-consistently, as K^D depends on Ω_S .

As discussed by Hedin and Lundquist [37], W can rigorously be written as the sum of an electronic, W^{el} , and ionic (or phonon), W^{ph} part, i.e., $W(\mathbf{r}, \mathbf{r}'; \omega) = W^{\text{el}}(\mathbf{r}, \mathbf{r}'; \omega) + W^{\text{ph}}(\mathbf{r}, \mathbf{r}'; \omega)$. In standard BSE calculations, W^{ph} is ignored while W^{el} is routinely computed within the random-phase approximation (RPA) [43, 44], neglecting the frequency dependence. The W^{ph} term may be written in the form (see SI [40])

$$W^{\text{ph}}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{\mathbf{q}\nu} D_{\mathbf{q}\nu}(\omega) g_{\mathbf{q}\nu}(\mathbf{r}) g_{\mathbf{q}\nu}^*(\mathbf{r}'), \quad (3)$$

where $D_{\mathbf{q}\nu}(\omega)$ is the phonon propagator and $g_{\mathbf{q}\nu}(\mathbf{r})$ is the electron-phonon vertex, encoding the probability amplitude for an electron at $\mathbf{r}$ to scatter off a phonon with crystal momentum $\mathbf{q}$ and branch index ν (see SI [40]) [37].

Incorporating W^{ph} into the BSE kernel, we obtain the phonon contribution to the real part of the direct electron-hole kernel matrix elements as follows (written here in the exciton

basis; see SI for details [40]):

$$\text{Re}[K_{SS'}^{\text{ph}}(\Omega)] = - \sum_{\substack{c\mathbf{v}\mathbf{k} \\ c'\mathbf{v}'\mathbf{k}'\nu}} A_{c\mathbf{v}\mathbf{k}}^{S*} g_{c\mathbf{c}'\nu}(\mathbf{k}', \mathbf{q}) g_{v\mathbf{v}'\nu}^*(\mathbf{k}', \mathbf{q}) A_{c'\mathbf{v}'\mathbf{k}'}^S \times \left[\frac{1}{\Omega - \Delta_{c'\mathbf{k}'v\mathbf{k}} - \omega_{\mathbf{q}\nu}} + \frac{1}{\Omega - \Delta_{c\mathbf{k}v'\mathbf{k}'} - \omega_{\mathbf{q}\nu}} \right], \quad (4)$$

where $g_{nm\nu}(\mathbf{k}', \mathbf{q}) = \langle m\mathbf{k}' + \mathbf{q} | g_{\mathbf{q}\nu} | n\mathbf{k}' \rangle$, with $\mathbf{q} = \mathbf{k} - \mathbf{k}'$. From Brillouin-Wigner perturbation theory, it follows that the change in the exciton energy, $\Delta\Omega_S$, due to phonon screening, is related to K^{ph} through $\Delta\Omega_S = \text{Re}[K_{SS}^{\text{ph}}(\Omega_S + \Delta\Omega_S)]$, in the limit where off-diagonal components of K^{ph} can be neglected.

We pause to note that W^{ph} should, in principle, be included in both the BSE kernel and *GW* self-energy. The contribution to the latter, i.e., iGW^{ph} , is equivalent to the Fan-Migdal electron-phonon self-energy [21], and leads to polaronic mass enhancement and energy renormalization (e.g. [45]) effects that would naively tend to increase the exciton binding energy over the bare or phonon-screened values. However as discussed in Ref. [10], interference between electron and hole polaron clouds upon overlap (hereafter referred to as “interference effects”) can counter mass enhancement effects, reducing the overall binding energy. A full *ab initio* study of bound electron-hole polarons, including the competition between mass enhancement and interference effects, as described by higher-order or self-consistent terms in the BSE kernel, requires a separate study and is beyond the scope of this work; thus, we restrict our focus here to quantifying and understanding the phonon screening contribution to the exciton binding energy, building on prior work [31, 33] and the standard *GW* approximation in all cases.

We now apply Eqs. 1 and 2, as implemented in the BerkeleyGW code [46], to CsPbX₃ lead halide perovskites, with X = Cl, Br, I. In Table 1 we compare calculated G_0W_0 band gaps and reduced effective masses to experiment. The computed gaps consistently underestimate experiment by up to 0.5 eV (see Table S2 of the SI [40]), a shortcoming of one-shot G_0W_0 approximation previously identified in a number of computational studies [18, 47–49]. Furthermore, the reduced effective masses of CsPbI₃ and CsPbBr₃ agree well with recent magneto-optical measurements at high magnetic fields, while for CsPbCl₃ the reduced mass is slightly underestimated with respect to experiment [8, 50]. In the same table we also report exciton binding energies calculated within the standard BSE approach, including only electronic screening when constructing the electron-hole kernel. In agreement with previous calculations [32, 33], we find that exciton binding energies neglecting phonon screening overestimate experiment by up to a factor of 3. Despite these discrepancies, after blue-shifting the calculated optical absorption spectrum to align with experiment, we find the lineshape to be in good agreement with measurements at low temperature (Figure 1a for CsPbCl₃ and Figure S2 for CsPbBr₃ and CsPbI₃).

We further observe that low-lying optical excitations are well described using a Mott-Wannier hydrogen model. In Figure 1b we compare the BSE solutions for the 1s and 2s exci-

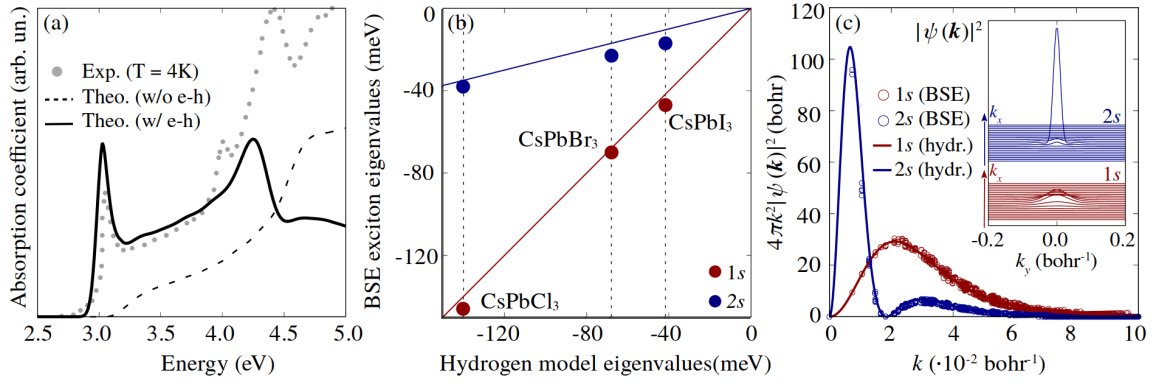


Figure 1. (a) Optical absorption spectrum calculated within GW/BSE (continuous line), RPA (dotted line), and from experiment (grey dots) [39] for $CsPbCl_3$. Calculated spectra are blue-shifted by 0.3 eV to match the experimental onset from Ref. 39. See SI for similar spectra for $CsPbBr_3$ and $CsPbI_3$ [40] (b) Exciton binding energies predicted from GW/BSE (filled circles) and the hydrogen model (lines). (c) Exciton radial probability density (main) and probability of localization (inset) in reciprocal space, calculated from GW/BSE and the hydrogen model for 1s (dark red) and 2s (dark blue) states.

tonic states with those predicted by the hydrogen model with μ calculated from G_0W_0 band structure, and with ϵ_∞ calculated within the RPA [43, 44]. We find a maximum difference between the hydrogenic model and the standard BSE calculations of 6 meV for both 1s and 2s excitonic energies across all three halide perovskites. Furthermore, in Figure 1c, we find that the excitonic wave functions calculated with BSE are accurately described by the hydrogenic model.

We now investigate how including phonon screening contributions shifts the energy of the lowest bound exciton by explicitly computing K^{ph} . We make two approximations to Eq 4: we use the analytic hydrogenic expressions for the exciton coefficients $A_{cv\mathbf{k}}^S$, and we approximate the electron-phonon matrix elements using a multi-mode, *ab initio* Fröhlich vertex, introduced in Ref. [38]:

$$g_{\mathbf{q}\nu} = i \frac{4\pi}{V} \sum_{\kappa} \left(\frac{1}{2NM_{\kappa}\omega_{\mathbf{q}\nu}} \right)^{1/2} \frac{\mathbf{q} \cdot \mathbf{Z}_{\kappa} \cdot \mathbf{e}_{\kappa\nu}(\mathbf{q})}{\mathbf{q} \cdot \epsilon_\infty \cdot \mathbf{q}}, \quad (5)$$

where V is the unit cell volume, M_{κ} are the atomic masses, $\mathbf{Z}_{\kappa}$ Born effective charge tensor and $\mathbf{e}_{\kappa\nu}(\mathbf{q})$ are the eigenvectors corresponding to the phonon modes $\omega_{\mathbf{q}\nu}$ for each atom indexed by κ . With the above simplifications, Eq. 4 becomes:

$$\Delta\Omega_S = -\frac{8a_0^3}{\pi^2} \sum_{\mathbf{k}\mathbf{q}\nu} \frac{|g_{\mathbf{q}\nu}|^2}{[1 + a_0|\mathbf{k}|^2][1 + a_0^2|\mathbf{k} + \mathbf{q}|^2]} \times \left[\frac{1}{\Omega_S - \Delta_{c\mathbf{k}\nu'\mathbf{k}+\mathbf{q}} - \omega_{\mathbf{q}\nu}} + \frac{1}{\Omega_S - \Delta_{c'\mathbf{k}+\mathbf{q}\nu\mathbf{k}} - \omega_{\mathbf{q}\nu}} \right], \quad (6)$$

where a_0 is the exciton Bohr radius. In principle, Ω_S appearing in the energy denominator above should be replaced with $\Omega_S + \Delta\Omega_S$ and the equation should be solved self consistently. In practice, for $CsPbX_3$ we find the above expression differs by less than 1 meV from the self-consistent solution justifying a “one-shot” approach. Finally, by definition, the change in the exciton binding energy is $\Delta E_B = -\Delta\Omega_S$.

The standard BSE exciton binding energies and phonon screening corrections are summarized in Table 1 for all three $CsPbX_3$ perovskites. We find that phonon screening contributes to the reduction of the exciton binding energy between 12% and 17% for the $CsPbX_3$ series, improving the agreement with measurements reported in Refs. [53, 54, 56]. However,

for $CsPbI_3$, our calculated relative phonon screening correction of 17% is less than half of the 50% correction predicted in Ref. [33]; as we show in the following, this discrepancy can be attributed to electronic band dispersion contributions, accounted for here but neglected in prior work.

To further investigate the contribution of phonon screening to the exciton binding energy, we perform a spectral decomposition on the phonon kernel (see Figure S4 of the SI [40]). For all three halide perovskites (see SI [40]), we find that the contribution of the highest lying IR active phonons accounts for more than 90% of the expectation value of K^{ph} , with the remaining contribution due to the lower energy LO modes. Furthermore, as shown in Figure S4, the phonon kernel drops sharply outside of the $\mathbf{q} \rightarrow 0$ range, a trend attributed to the strong localization of the exciton wave function around the center of the Brillouin zone, and the fast decay of the long-range electron-phonon vertex in reciprocal space.

Given the flat profile of the optical phonon band shown in Figure. S4, we can further simplify the phonon kernel by replacing the phonon frequencies with ω_{LO} , and approximating the electron-phonon vertex in Eq. 6 using the Fröhlich model [58], $|g_{\mathbf{q}}^F|^2 = 4\pi\omega_{LO}/(2NV)(\epsilon_\infty^{-1} - \epsilon_0^{-1})/q^2$, where N is the total number of unit cells in the crystal. This approximation yields a change in the phonon screening correction of $\sim 1\%$ with respect to the *ab initio* result, indicating that the single dispersionless phonon model is a suitable approximation for the phonon kernel in these systems. Assuming isotropic and parabolic electronic band dispersion, Eq. 6 can be solved analytically (see the SI for details [40]), obtaining:

$$\Delta E_B = -2\omega_{LO} \left(1 - \frac{\epsilon_\infty}{\epsilon_0} \right) \frac{\sqrt{1 + \omega_{LO}/E_B} + 3}{(1 + \sqrt{1 + \omega_{LO}/E_B})^3}. \quad (7)$$

For isotropic semiconductors, Eq. 7 yields very close agreement with the numerical result (see Table S4 of the SI [40]).

Since the exciton wave function is highly localized at the center of the Brillouin zone (see Fig. S4 of the SI [40]), it is tempting to assume that the dispersion of the electronic band structure may also be neglected. This approximation leads to an even simpler expression for the change in the exciton binding energy, $\Delta E_B = -2E_B \frac{\omega_{LO}}{\omega_{LO} + E_B} (1 - \epsilon_\infty/\epsilon_0)$ (see

	ω_{LO} (meV)	ω_{LO}^{exp} (meV)	E_B (meV)	ΔE_B (meV)	E_B^{exp} (meV)	μ (m_e)	μ^{exp} (m_e)	ε_∞	ε_∞^{exp}	ε_0	ε_0^{exp}
CsPbCl ₃	26	25.3/28.0 ^a ; 27.5 ^b	146	-17	72 $\pm$ 3 ^c ; 64 $\pm$ 1.5 ^d	0.142	0.202 $\pm$ 0.01 ^d	3.7	3.7 ^a	17.5	15.7 ^a
CsPbBr ₃	18	17.9/20.4 ^e	70	-12	33 $\pm$ 1 ^f ; 38 $\pm$ 3 ^c	0.102	0.126 $\pm$ 0.02 ^f	4.5	N/A	18.6	N/A
CsPbI ₃	14	14.2 ^g	47	-8	15 $\pm$ 1 ^f	0.093	0.114 $\pm$ 0.01 ^f	5.5	N/A	22.5	N/A

Table 1. Calculated LO phonon frequencies (ω_{LO}), bare exciton binding energies (E_B), phonon screening corrections (ΔE_B), reduced effective masses (μ), static (ε_0 from DFPT) and optical dielectric constants (ε_∞ from DFPT and G_0W_0), and corresponding experimental data from Refs. ^a[51]; ^b[52]; ^c[53]; ^d[54]; ^e[55]; ^f[56]; ^g[57].

SI [40]); however, we find that it overestimates the magnitude of the phonon screening contribution by up to 50% with respect to the *ab initio* result for these systems.

To examine phonon screening trends across a wide range of semiconductors and insulators, we plot the phonon kernel relative to the bare exciton binding energy E_B , $|\Delta E_B|/E_B$, as a function of E_B/ω_{LO} , and $\varepsilon_0/\varepsilon_\infty$, in Figure 2, following Eq. 7. We overlay our calculations for the CsPbX₃ series, as well as some other isotropic semiconductors and insulators such as CdS, GaN, AlN and MgO (see SI for computational details [40]). In all cases considered, the inclusion of phonon screening effects reduces the exciton binding energy significantly, bringing calculated values in closer agreement with experiment.

Particularly for halide perovskites, our calculations reconcile prior reports, and clearly establish the importance of phonon screening effects for excitons in halide perovskites, in agreement with Ref. [33]. However, corrections due to phonon screening do not fully account for the discrepancy between calculated and measured exciton binding energies. Considering the systematic overestimation of exciton binding energies for all systems beyond halide perovskites, we expect that the net contribution of polaronic mass enhancement [45] and interference effects [10] will further reduce the exciton binding energies and improve the agreement with experiment, as proposed by Ref. [10, 11] for MgO and several other semiconductors. However, G_0W_0 -BSE calculations of halide perovskites are known to exhibit a strong dependence to the mean-field starting point [48], and the electron-phonon matrix elements, computed starting from the standard Kohn-Sham eigensystem may underestimate couplings obtained from higher level theory [59–61]. Therefore, a detailed benchmarking of these effects is required, in addition to simply including polaronic effects. While we reserve this detailed analysis to future studies, we emphasize that the relative phonon screening correction derived in this study is robust, and the formalism introduced here is independent of the choice of computational setup.

As a general trend, Figure 2 highlights that the magnitude of the phonon screening correction increases as the ratio E_B/ω_{LO} decreases, and in systems with a large static dielectric constant. Further, all parameters appearing in Eq. 7 and depicted in Figure 2 can be readily computed or measured experimentally so that this simplified picture can be used in both theoretical and experimental contexts to directly assess the expected phonon screening correction to the bare exciton binding energy, and identify systems for which phonon screening is expected to be significant.

In summary, we generalized the *ab initio* Bethe-Salpeter equation approach to include both electronic and phonon contributions to the screened Coulomb interaction, W , and studied phonon screening effects on the electron-hole interactions in halide perovskites and other important semiconductors. We showed that *ab initio* BSE calculations including phonon screening can reduce the exciton binding energy of lead-halide perovskites significantly as compared to electronic screening alone, reconciling two previous contradictory hypotheses on the importance of phonon screening in metal-halide perovskites. We rationalized our results by generalizing the Wannier-Mott model for excitons in a phonon-screened environment. Within this model, we showed that phonon screening is important for other semiconductors, and can be traced back to four material specific parameters, μ , ω_{LO} , ε_∞ and ε_0 . We derived a simple expression providing intuition for the importance of lattice vibrations on the excitonic properties of materials and outlined a general, simple, and quantitative approach to estimate the exciton binding energy correction using physical quantities that can be readily calculated theoretically or measured experimentally. By introducing a general framework to quantitatively account for phonon screening in *ab initio* BSE calculations, our study clarifies the importance of phonon screening corrections, and provides a necessary foundation for future treatment of polarons and higher order

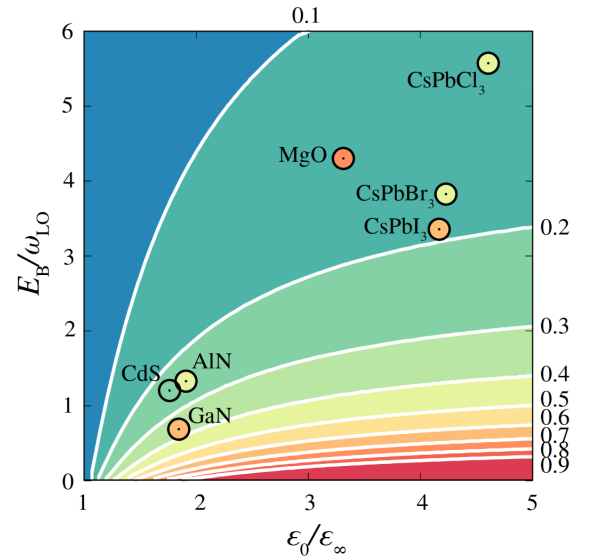


Figure 2. Color map of $\Delta E_B/E_B$, calculated using Eq. 7, as a function of $\varepsilon_0/\varepsilon_\infty$ and E_B/ω_{LO} . The isoline values are marked at the upper and rightmost edge of the plot. The color of each circle corresponds to the ratio $(E_B - E_B^{exp})/E_B$, as read on the color map. Calculated and experimental exciton binding energies are summarized in Table S4.

processes beyond two particle excitations for these and other complex materials.

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