

Pairing of vibronic small excitons due to enhanced polarizability in a crystalline polarizable nonmetallic medium

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Parity breaking at a centrosymmetric site, resulting in the appearance of an inversion electric dipole moment, is shown to enhance the polarizability and thus add an additional binding energy for the pairing of vibronic excitons into biexcitons. Implications of such formation of biexcitons in polarizable media like alkali halides are discussed. The possibility of electron-hole binding in layered perovskites, where the electron and hole move in the neighboring conducting planes, while binding is mediated by a highly polarizable partner in the intercalated insulating layer, is also considered.

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I. INTRODUCTION

The binding of a pair of excitons into biexcitons in crystalline semiconductors has been well established for many years.^{1,2} It has now become rather common to observe biexcitons in quantum wells, because of their enhanced binding energy due to confinement.³ The binding energy of biexcitons in GaAs quantum wells has been systematically measured⁴ and calculated theoretically.^{5,6} However, previous theories of the binding of biexcitons both in bulk semiconductors and quantum wells have taken only the Coulomb interaction among the carriers to be responsible for the binding of biexcitons.

In polarizable media, like for instance ionic crystals, the situation may be regarded to be different because excitons are polarizable electrostatically even though they are neutral. They may thus be expected to couple to an external electric field through permanent or induced dipoles. In a previous paper,⁷ we showed that off-centered vibronic excitons may be formed if the original site symmetry-operations incorporate the spatial inversion. Thus the appearance of an off-centered exciton at a site breaks down the local parity conservation, which allows the exciton to acquire an extra electric dipole moment. These off-center dipoles and the resulting vibronic polarizabilities can then open channels of binding of excitons into biexcitons through their vibronic dispersive forces.

It is well known that a renormalized vibronic polarizability may define the electrostatic response of strongly coupled electron-phonon systems; a familiar example is the ammonia molecule. Moreover, the peculiar behavior of small polarons coupled to asymmetric modes was already expressed by Holstein,⁸ who showed that the coupling to an asymmetric intramolecular vibration could split the vibronic potential into a double-well type. Now that the quantum-mechanical interpretation of the inversion spectrum is based on the pseudo-Jahn-Teller effect (PJTE), it predicts renormalized vibronic polarizabilities for the ammonia molecules.⁹ Subsequent developments in theory have transferred the vibronic concept to off-centered polarons.¹⁰

Although the possibility of pairing excitons through

dipole-dipole coupling was clearly indicated earlier,¹¹ the renormalization of polarizabilities due to exciton-phonon coupling has not yet been studied. In order to address this problem, in this paper, we first calculate the electrical polarizability of an off-centered exciton system and compare it with that of an on-centered exciton system. Pair interactions of polarizable vibronic Frenkel excitons are then introduced, and the resulting renormalized polarizabilities are derived. For providing quantitative estimates, the vibronic polarizabilities and binding energies, thus derived, are calculated numerically for alkali halides. We also consider the possibility that an electron and a hole, moving in neighboring conducting planes in a layered perovskite, would pair by binding separately to a highly polarizable partner in the intercalated insulating layer. The theory can be applied to low-dimensional structures as well. The results of this study are expected to advance our understanding of the nonlinear photonic properties of polarizable systems.

The paper is organized as follows. In Sec. II, we present the derivation of the binding energy as a function of the polarizability of an exciton interacting with phonons and an external electric field. In Sec. III, an expression for the renormalized or vibronic polarizability of an exciton due to its interaction with phonons and external electric field is derived. The ratio of the renormalized polarizability to that of the electronic polarizability (without phonon interaction), and the temperature dependence of the vibronic polarizability at higher temperatures, are also derived in Sec. III. In Sec. IV, an expression for the dipole-dipole interaction between a pair of vibronic excitons (excitons interacting with phonons), and its contribution to the binding energy of a resulting biexciton, are derived. In Sec. V we present the binding energy of a pair of electron and hole confined in one layer mediated by a polarizable partner localized in another layer in a layered material. In Sec. VI, we discuss the results obtained.

II. ELECTRIC-FIELD COUPLING

In order to study an electric field coupling with an exciton, we first develop a theory of coupling between the quantized field of excitons and an extra charge e_I , localized at a site I . For the localized nature of the problem, it is more

convenient to express the Hamiltonian of an exciton interacting with the lattice in the real crystal space, and express the wave functions in terms of Wannier's localized representation. The Hamiltonian of an exciton interacting with phonons in a crystal can thus be written^{7,12} as

$$H = \sum_{ij\alpha\beta s} T_{ij\alpha\beta s} B_{i\alpha s}^\dagger B_{j\beta s} + \sum_{i\alpha s} E_{i\alpha s} B_{i\alpha s}^\dagger B_{i\alpha s} + H_{Iph}, \quad (1)$$

where H_{Iph} is given by

$$H_{Iph} = \sum_{i\alpha\beta s} G_{i\alpha\beta s} Q_{i\alpha\beta} B_{i\alpha s}^\dagger B_{i\beta s} + \frac{1}{2} \sum_{i\alpha\beta} \left(\frac{P_{i\alpha\beta}^2}{M_{i\alpha\beta}} + K_{i\alpha\beta} Q_{i\alpha\beta}^2 \right), \quad (2)$$

where the subscripts i and j label lattice sites, α and β are exciton bands, and s is the spin. $P_{i\alpha\beta}$, $M_{i\alpha\beta}$, and $K_{i\alpha\beta}$ are the momentum, reduced mass, and force constant, respectively, associated with the lattice vibration mode corresponding to the lattice displacement coordinate $Q_{i\alpha\beta}$. $G_{i\alpha\beta s}$ is the linear exciton-phonon coupling coefficient. We adopt a simple model of excitons in two nearly degenerate narrow bands α and β , and assume G , K , E_α , and E_β to be independent of the site and spin. Using the adiabatic approximation, that means neglecting the kinetic-energy operators of ions, and the eigenvalues $E_{AD\pm}(Q)$ and eigenvectors $|AD\pm; Q\rangle$ of the Hamiltonian in Eq. (1) are obtained as⁷

$$E_{AD\pm}(Q) = W_\alpha(\mathbf{k}) + \frac{1}{2} \{ KQ^2 \pm [(2GQ)^2 + E_{\alpha\beta}^2]^{1/2} \}, \quad (3)$$

where $W_\alpha(\mathbf{k})$ is the dispersion energy term of an exciton in the energy state α and wave vector \mathbf{k} , and

$$E_{\alpha,\beta} = E_\alpha - E_\beta. \quad (4)$$

It is to be noted that the dispersion energy $W_\alpha(\mathbf{k})$ plays no role in a problem of localized nature such as that considered here, and therefore it will be dropped from further calculations. The corresponding eigenvectors can be expressed as

$$|AD\pm; Q\rangle = \sum_{i\alpha s} c_{i\alpha s\pm} B_{i\alpha s}^\dagger |0\rangle, \quad (5)$$

where

$$c_{i\alpha s\pm} = -\frac{1}{2}^{1/2} [-\cos(f_{i\alpha\beta}/2) \pm \sin(f_{i\alpha\beta}/2)], \quad (6)$$

$$c_{i\beta s\pm} = \frac{1}{2}^{1/2} [\pm \cos(f_{i\alpha\beta}/2) + \sin(f_{i\alpha\beta}/2)], \quad (7)$$

and

$$f_{i\alpha\beta} = \tan^{-1}(E_{\alpha\beta}/2GQ). \quad (8)$$

The sign \pm refers to the upper and lower adiabatic branches of the energy eigenvalues, and the corresponding eigenvectors are functions of the vibrational coordinate Q .

The interaction operator H' between the extra charge and the exciton field can be written as

$$H' = \sum_{ij\alpha\beta s} W(ij|\alpha\beta) B_{i\alpha s}^\dagger B_{j\beta s}, \quad (9)$$

where $B_{i\alpha s}^\dagger$ ($B_{i\alpha s}$) are exciton creation (annihilation) operators, and the coupling constant $W(ij|\alpha\beta)$ is given by¹³

$$W(ij|\alpha\beta) = (e_I e / \kappa) \int w_\alpha(\mathbf{r} - \mathbf{r}_i) |\mathbf{r} - \mathbf{r}_j|^{-1} w_\beta(\mathbf{r} - \mathbf{r}_j) d\mathbf{r}. \quad (10)$$

Here κ is the dielectric constant, and $w_\alpha(\mathbf{r} - \mathbf{r}_i)$ are Wannier's functions of the host lattice. For calculating the coupling constant $W(ij|\alpha\beta)$ in Eq. (10), we apply the coordinate transformation $\mathbf{r} - \mathbf{r}_i = \mathbf{u}_i$, $\mathbf{r}_j - \mathbf{r}_i = \mathbf{R}_i$, and set $j = i$, because of the negligible overlap of Wannier's functions at different sites. We then use a multiple expansion as

$$|\mathbf{r} - \mathbf{r}_j|^{-1} = |\mathbf{u}_i - \mathbf{R}_i|^{-1} \sim R_i^{-1} (1 + \mathbf{u}_i \cdot \mathbf{R}_i / R_i^2) + \dots. \quad (11)$$

Terminating the series at the dipole terms for $u_i \ll R_i$ and then using Eq. (11) in Eq. (10), we obtain

$$\begin{aligned} W(ii|\alpha\beta) &= (e_I e / \kappa R_i) \delta_{\alpha\beta} + (e_I \mathbf{R}_i / \kappa R_i^3) \cdot \mathbf{p}_{i\alpha\beta} \\ &= e U_i \delta_{\alpha\beta} + \mathbf{p}_{i\alpha\beta} \cdot \mathbf{F}_i, \end{aligned} \quad (12)$$

where $U_i = e_I / \kappa R_i$ is the monopole-monopole interaction term, and $\mathbf{F}_i = (e_I \mathbf{R}_i / \kappa R_i^3)$ is the field created by the extra charge. $\mathbf{p}_{i\alpha\beta}$ is an α - β mixing dipole given by

$$\mathbf{p}_{i\alpha\beta} = \int w_\alpha^*(\mathbf{u}_i) e \mathbf{u}_i w_\beta(\mathbf{u}_i) d\mathbf{u}_i. \quad (13)$$

For a distant charge e_I the intraband monopole-monopole terms cancel out on summing for the electron and hole at site i , and then we obtain

$$W(ii|\alpha\beta) = \mathbf{p}_{i\alpha\beta} \cdot \mathbf{F}_i. \quad (14)$$

Considering H' as a perturbation operator and then using Eq. (14) in Eq. (9), we obtain its first-order contribution to the energy of the lower adiabatic branch $E_{AD-}(Q)$ as

$$\begin{aligned} \langle H' \rangle &= \sum_{i\alpha\beta} \langle AD-; Q | H'_{i\alpha\beta} | AD-; Q \rangle \\ &= 2 \sum_{i\alpha\beta} W(ii|\alpha\beta) c_{i\alpha-}^* c_{i\beta-} \\ &= \sum_{i\alpha\beta} \mathbf{p}_{i\alpha\beta} \cdot \mathbf{F}_i \cos(f_{i\alpha\beta}) = \sum_{i\alpha\beta} \mathbf{p}_{i\alpha\beta}(Q) \cdot \mathbf{F}_i, \end{aligned} \quad (15)$$

where

$$\mathbf{p}_{i\alpha\beta}(Q) \equiv \mathbf{p}_{i\alpha\beta} \cos(f_{i\alpha\beta}) = \mathbf{p}_{i\alpha\beta} \{ 2GQ / [(2GQ)^2 + E_{\alpha\beta}^2]^{1/2} \} \quad (16)$$

is the adiabatic off-center dipole at Q . As the overlap between the Wannier's functions at different sites is negligible, the individual terms of Eq. (15) will be the same and hence independent of site i . Therefore, we will drop the subscript i from the expression of $\langle H' \rangle$ given in Eq. (15), and denote the individual site expectation values as the average $\langle H' \rangle_{av}$ given by

$$\langle H' \rangle_{av} = \mathbf{p}_{\alpha\beta}(Q) \cdot \mathbf{F}. \quad (17)$$

From Eq. (16), one finds that when the vibrational coordinate oscillates between $-Q$ and Q across the interwell barrier,

the adiabatic dipole $\mathbf{p}_{\alpha\beta}$ oscillates between $-\mathbf{p}_{\alpha\beta}$ and $\mathbf{p}_{\alpha\beta}$, so that its average value vanishes. Thus the dipole has an elastolectric character.

According to the adiabatic approximation, the excitonic energy thus derived in Eqs. (3) and (15) acts as a potential-energy term for the nuclei in the vibronic Hamiltonian for solving the vibronic eigenvalue problem. However, as the expression of the adiabatic dipole in Eq. (16) is quite complicated, we will rather follow a circumventing way by replacing $P_{vv'}$ with its average value in the vibronic ground state as an approximation. The average of Eq. (16) in the harmonic-oscillator ground state $u_g(Q \pm Q_o)$ centered at $\pm Q_o$ is obtained as⁷

$$\pm \mathbf{P}_{\alpha\beta}(Q_o) = \pm \mathbf{p}_{\alpha\beta} [1 - (E_{\alpha\beta}/4E_{JT})^2]^{1/2}, \quad (18)$$

where $E_{JT} = G^2/2K$. This average value of the dipole is only meaningful at $4E_{JT}/E_{\alpha\beta} > 1$. Actually the dipole ascends from nil at the mode-softening point ($4E_{JT} = E_{\alpha\beta}$) to $\mathbf{p}_{\alpha\beta}$ of Eq. (13) in the small-radius excitonic polaron extreme where $4E_{JT}/E_{\alpha\beta} \gg 1$. Using Eq. (18) in Eq. (17), we obtain the average of the interaction in the ground state as

$$\langle H' \rangle_{av} = -\mathbf{p}_{\alpha\beta}(Q_o) \cdot \mathbf{F}, \quad (19)$$

where the negative sign refers to the lower value for the ground state. We will now study the combined effect of the exciton-lattice interaction and electric field by calculating the eigenvalues of the vibronic Hamiltonian $\langle H' \rangle_{av}$, given by

$$H_{vib} = H_{vib,o} + \langle H' \rangle_{av}, \quad (20)$$

where $H_{vib,o}$ is the vibronic Hamiltonian obtained by adding the kinetic-energy operator in Eq. (3) as

$$H_{vib,o} = -(\hbar^2/2M)(d^2/dQ^2) + \frac{1}{2}\{KQ^2 - [(2GQ)^2 + E_{\alpha\beta}^2]^{1/2}\}. \quad (21)$$

For calculating the energy eigenvalue of Eq. (20), we introduce a basis composed of the symmetric and antisymmetric combinations of vibronic wave functions $u_g(Q - Q_o)$ and $u_g(Q + Q_o)$; in this basis only the field-coupling terms are off-diagonal. We thus solve the Schrödinger equation

$$H_{vib}|u_g(Q - Q_o) \pm u_g(Q + Q_o)\rangle = E_{vib\pm}(F)|u_g(Q - Q_o) \pm u_g(Q + Q_o)\rangle \quad (22)$$

to obtain the energy eigenvalue $E_{vib\pm}(F)$ as

$$E_{vib\pm}(F) = \frac{1}{2}\{H_{SS}/(1+S) + H_{AA}/(1-S) \pm [\{H_{SS}/(1+S) - H_{AA}/(1-S)\}^2 + 4H'_{SA}H'_{AS}/(1-S^2)]^{1/2}\}, \quad (23)$$

where the matrix elements are⁷

$$\begin{aligned} H_{SS} &= H_{RR} + H_{RL}, & H_{AA} &= H_{RR} - H_{RL}, \\ H_{RR} &= \langle u_g(Q - Q_o) | H_{vib,o} | u_g(Q - Q_o) \rangle, \\ H_{LL} &= \langle u_g(Q + Q_o) | H_{vib,o} | u_g(Q + Q_o) \rangle, \\ H_{RL} &= \langle u_g(Q - Q_o) | H_{vib,o} | u_g(Q + Q_o) \rangle, \\ H_{LR} &= \langle u_g(Q + Q_o) | H_{vib,o} | u_g(Q - Q_o) \rangle, \\ H'_{SA} &= H'_{AS} = \mathbf{P}_{\alpha\beta}(Q_o) \cdot \mathbf{F}. \end{aligned} \quad (24)$$

Here we have used $H_{RR} = H_{LL}$ and $H_{RL} = H_{LR}$, and $S = \langle u_g(Q + Q_o) | u_g(Q - Q_o) \rangle$ is the overlap integral. From Eqs. (23) and (24) we obtain the energy-level (tunneling) splitting $\delta E_{vib}(F)$ as:

$$\delta E_{vib}(F) \equiv E_{vib-}(F) - E_{vib+}(F) = \{[\delta E_{vib}(0)]^2 + [2\mathbf{p}_{\alpha\beta}(Q_o) \cdot \mathbf{F}]^2/(1-S^2)\}^{1/2}, \quad (25)$$

where $\delta E_{vib}(0)$ is the splitting at the zero field but at nonzero exciton-lattice interaction given by⁷

$$\delta E_{vib}(0) = (E_{\alpha\beta}/2) \left[1 - \frac{E_{\alpha\beta}}{4E_{JT}} \right] / \sinh \left[\frac{2E_{JT}}{\hbar\omega} \left[1 - \left(\frac{E_{\alpha\beta}}{4E_{JT}} \right)^2 \right] \right]. \quad (26)$$

The polaron binding energy $E_p(F)$ is given by

$$E_p(F) \equiv \frac{1}{2}(E_{vib+} + E_{vib-}) = E_p(\mathbf{0}). \quad (27)$$

Thus the tunneling splitting $\delta E_{vib}(F)$ in Eq. (25) is modified due to the interaction with the external electric field, but the polaron binding energy $E_p(F)$ in Eq. (27) is independent of \mathbf{F} . Accordingly, as \mathbf{F} increases, the tunneling splitting is wid-

ened without affecting the polaron binding energy. The corresponding quantities at the zero field can be obtained from Ref. 7.

The field-dependent term in Eq. (25) is the monopole-induced dipole coupling potential. As the polaron binding energy is the same whether the field is on or off, the difference $\delta E_{vib}(F) - \delta E_{vib}(\mathbf{0})$, obtained from Eq. (25), can be regarded as a monopole-induced dipole binding energy, $U_{bind,vib}$, obtained as

$$U_{bind,vib} = \frac{1}{4}[\delta E_{vib}(\mathbf{F}) - \delta E_{vib}(\mathbf{0})], \quad (28)$$

which for $2\mathbf{p} \cdot \mathbf{F} \ll \delta E_{vib}(0)$, and $S^2 \ll 1$ reduces to

$$U_{bind,vib} \sim \frac{1}{2}[\mathbf{p}_{\alpha\beta}(Q_o) \cdot \mathbf{F}]^2 / \delta E_{vib}(0) \equiv (1/2)\alpha_{vib}F^2, \quad (29)$$

where the factor 1/4 is introduced to obtain the correct form for the binding energy, and α_{vib} is the vibronic polarizability⁹ given by

$$\alpha_{vib} = [\mathbf{p}_{\alpha\beta}(Q_o) \cos(\mathbf{p}_{\alpha\beta}, \mathbf{F})]^2 / \delta E_{vib}(0), \quad (30)$$

where the cosine term should be regarded as averaged over all field-dipole angles. Equation (29) has the form of the interaction energy between a polarizable particle with an external electric field to which it couples through the induced dipole of magnitude $\alpha_{vib}F$.

Near the onset of an off-center instability ($4E_{JT} \sim E_{\alpha\beta}$), the local vibronic dipole [Eq. (13)] is virtually smeared due to interwell tunneling. Such a smearing usually affects the configurational averaging of any Q -dependent quantum-mechanical quantity over the off-center sites. Nevertheless the exciton is still polarizable in an external electric field like a polarizable s atom. However, at the other extreme ($4E_{JT} \gg E_{\alpha\beta}$), the vibronic exciton being virtually localized in one of the lower-symmetry wells at $\pm Q_o$, it will have associated with it a nonvanishing dipole moment $\pm p(Q_o)$. Consequently, its behavior may now be more like a rigid dipolar molecule. Thus, in both cases, two nearby excitons, whether polarizable or dipolar, may be expected to couple to each other to form a biexciton through the dipolar forces and with a significant binding energy. This binding energy is in addition to the Coulombic one, and it is nonzero in a polarizable medium as shown below.

$$\begin{aligned} \langle E(\mathbf{F}) \rangle &= [E_{vib+} \exp(-E_{vib+}/k_B T) + E_{vib-} \exp(-E_{vib-}/k_B T)] / [\exp(-E_{vib+}/k_B T) + \exp(-E_{vib-}/k_B T)] \\ &= -[\delta E_{vib}(0) \tanh(\delta E_{vib}(0)/2k_B T) + \alpha_{vib}F^2 + \dots]. \end{aligned} \quad (34)$$

The polarizability $\alpha_{vib}(T)$ is then given by the coefficient of the second-order term in F as:

$$\begin{aligned} \alpha_{vib}(T) &= (p_o^2/2k_B T) \{ (2k_B T / \delta E_{vib}(0)) \tanh(\delta E_{vib}(0)/2k_B T) \\ &\quad + [1/\cosh(\delta E_{vib}(0)/2k_B T)]^2 \}. \end{aligned} \quad (35)$$

In the low temperature limit, where $2k_B T \ll \delta E_{vib}(0)$, Eq. (35) gives the same result as that in Eq. (30), whereas in the higher-temperature limit when $2k_B T \gg \delta E_{vib}(0)$, we obtain the reorientational polarizability $\alpha_{or}(T)$ of a permanent-dipole rigid molecule given by

$$\alpha_{or}(T) = p^2/k_B T, \quad (36)$$

where p is the magnitude of the vibronic dipole given in Eq. (18). It is obvious that in the higher-temperature limit $\alpha_{or}(T)$

III. VIBRONIC POLARIZABILITIES

The vibronic polarizability, obtained in Eq. (30), may become significantly larger than the electronic polarizability α_{el} , which is obtained if the system is not coupled with the phonon field, but subjected only to the external field \mathbf{F} . In the present case of a two-level (α and β) system with an energy separation of $E_{\alpha\beta}$, we can write α_{el} in an analogous form to Eq. (30) as

$$\alpha_{el} = [\mathbf{p}_{\alpha\beta} \cos(\mathbf{p}, \mathbf{F})]^2 / E_{\alpha\beta}, \quad (31)$$

and following Eq. (29) the corresponding electronic monopole-induced dipole binding energy can be written as

$$U_{bind,el} = \frac{1}{2}\alpha_{el}F^2. \quad (32)$$

Using Eqs. (30) and (31), we can derive the ratio α_{vib}/α_{el} as⁷

$$\begin{aligned} \alpha_{vib}/\alpha_{el} &= 2 \sinh([2E_{JT}/\hbar\omega][1 - (E_{\alpha\beta}/4E_{JT})^2]) \\ &\quad \times [1 + E_{\alpha\beta}/4E_{JT}], \end{aligned} \quad (33)$$

which may become exponentially large for $4E_{JT} > E_{\alpha\beta} \gg \hbar\omega$. This suggests that the binding energy in the range of $4E_{JT} > E_{\alpha\beta} \gg \hbar\omega$ should be significantly enhanced in a polarizable medium.

As we have considered only the ground-state energies so far, the results obtained are applicable only at low temperatures. At higher temperatures, however, the temperature dependence of the vibronic polarizability can be derived by assuming the Boltzmann distribution in the occupation of splitted vibronic energy levels. Considering that the lower and higher-energy levels correspond to symmetric and anti-symmetric combination of wave functions, respectively, the average energy of the system in an applied field can be obtained as⁷

decreases as the temperature increases. These and higher-symmetry vibronic polarizabilities are discussed in Ref. 9.

IV. DIPOLE-DIPOLE PAIRING

Here we will assume that the vibronic exciton-exciton coupling is the same as a vibronic dipole-dipole coupling. In the localized limit the exciton-exciton interaction Hamiltonian H_{int} can be written as:

$$H_{int} = (1/2) \sum_{\alpha\beta\gamma\delta,ijkl} W(\alpha\beta\gamma\delta|ijkl) B_{i\alpha s}^\dagger B_{j\beta s}^\dagger B_{k\gamma s} B_{l\delta s}, \quad (37)$$

where i, j, k , and l denote lattice sites, α, β, γ , and δ denote exciton bands, s is the spin, and the coupling function $W(\alpha\beta\gamma\delta|ijkl)$ is given by

$$\begin{aligned}
W(\alpha\beta\gamma\delta|ijkl) &= \int w_\alpha^*(\mathbf{r}-\mathbf{r}_i)w_\beta^*(\mathbf{r}'-\mathbf{r}_j) \\
&\quad \times \{(e^2/k)|\mathbf{r}-\mathbf{r}'|^{-1}\} \\
&\quad \times w_\gamma(\mathbf{r}-\mathbf{r}_k)w_\delta(\mathbf{r}'-\mathbf{r}_l)d\mathbf{r}d\mathbf{r}'. \quad (38)
\end{aligned}$$

Defining $\mathbf{r}-\mathbf{r}_i=\mathbf{u}_i$, $\mathbf{r}'-\mathbf{r}_j=\mathbf{v}_j$, $\mathbf{r}_i-\mathbf{r}_j=\mathbf{R}_{ij}$, we can expand $|\mathbf{r}-\mathbf{r}'|^{-1}=|\mathbf{u}_i-\mathbf{v}_j+\mathbf{R}_{ij}|^{-1}$ into a multipole series. Here we consider only those displacements \mathbf{u}_i and \mathbf{v}_j that are both small ($u_i, v_j \ll R_{ij}$) and correlated ($\mathbf{u}_i \cdot \mathbf{R}_{ij} = \mathbf{v}_j \cdot \mathbf{R}_{ij}$), and then we obtain

$$\begin{aligned}
|\mathbf{r}-\mathbf{r}'|^{-1} &= R_{ij}^{-1}[1+(\mathbf{u}_i-\mathbf{v}_j)^2/R_{ij}^2]^{-1/2} \\
&\simeq R_{ij}^{-1}[1-(1/2R_{ij}^2)(\mathbf{u}_i-\mathbf{v}_j)^2]. \quad (39)
\end{aligned}$$

Assuming the vanishing overlap between Wannier's functions at neighboring sites, setting $k=j$ and $l=i$ (two sites) and using Eq. (39) in Eq. (38), we obtain:

$$\begin{aligned}
W(\alpha\beta\gamma\delta|ijji) &= U_{ij}\delta_{\alpha\delta}\delta_{\beta\gamma} - (1/2kR_{ij}^3) \\
&\quad \times \{q_{i\alpha\delta}\delta_{\beta\gamma} + q_{j\beta\gamma}\delta_{\alpha\delta} - 2\mathbf{p}_{i\alpha\delta} \cdot \mathbf{p}_{j\beta\gamma}\}, \quad (40)
\end{aligned}$$

where

$$U_{ij} = e^2/\kappa R_{ij}, \quad (41)$$

$$\mathbf{p}_{i\alpha\beta} = \langle w_\alpha(\mathbf{u}_i) | e\mathbf{u}_i | w_\beta(\mathbf{u}_i) \rangle, \quad (42)$$

and

$$q_{i\alpha\beta} = \langle w_\alpha(\mathbf{u}_i) | e^2\mathbf{u}_i^2 | w_\beta(\mathbf{u}_i) \rangle. \quad (43)$$

Because of symmetry, $\mathbf{p}_{i\alpha\beta}=\mathbf{0}$ for $\alpha=\beta$, and $q_{i\alpha\beta}=0$ for $\alpha \neq \beta$. In Eq. (40), setting $\gamma=\alpha$ and $\delta=\beta$, and using $\mathbf{p}_{i\alpha,\beta} = -\mathbf{p}_{i\beta,\alpha}$, we obtain a two-band coupling constant as

$$\begin{aligned}
W(\alpha\beta\alpha\beta|ijji) &= U_{ij}\delta_{\alpha\beta}\delta_{\alpha\beta} - [\mathbf{p}_{i\alpha\beta} \cdot \mathbf{p}_{j\alpha\beta}/\kappa R_{ij}^3] \\
&\quad - (1/2kR_{ij}^3)[q_{i\alpha\beta}\delta_{\beta\alpha} + q_{j\beta\alpha}\delta_{\alpha\beta}]. \quad (44)
\end{aligned}$$

The first term of Eq. (44) is the Coulomb repulsive energy term due to an intraband ($\alpha=\beta$) monomole-monopole interaction, and the second term is attractive due to the interband ($\alpha \neq \beta$) dipole-dipole interaction. The third term is the higher-order quadrupole intraband interaction, which tends to reduce the Coulomb repulsion.

Another interaction function is obtained for $\alpha=\beta$, and $\gamma=\delta$ as

$$\begin{aligned}
W(\alpha\alpha\gamma\gamma|ijji) &= U_{ij}\delta_{\alpha\gamma}\delta_{\alpha\gamma} + [\mathbf{p}_{i\alpha\gamma} \cdot \mathbf{p}_{j\alpha\gamma}/\kappa R_{ij}^3] \\
&\quad - (1/2kR_{ij}^3)[q_{i\alpha\gamma} + q_{j\alpha\gamma}]\delta_{\alpha\gamma}, \quad (45)
\end{aligned}$$

where the second term of the interband dipole-dipole interaction is now repulsive.

Two excitons, in different bands ($\alpha \neq \beta$), may pair due to the attractive dipole-dipole interaction $W(\alpha\beta\alpha\beta|ijji)$ in Eq. (44). The corresponding Hamiltonian for $\alpha \neq \beta$ can be written as

$$\begin{aligned}
H_{int} &= -\frac{1}{2} \sum_{i \neq j, \alpha \neq \beta} [(\mathbf{p}_{i\alpha\beta} \cdot \mathbf{p}_{j\alpha\beta}/\kappa R_{ij}^3) \\
&\quad \times B_{i\alpha s}^\dagger B_{j\beta s}^\dagger B_{j\alpha s} B_{i\beta s} + \text{H.c.}]. \quad (46)
\end{aligned}$$

Replacing H_{Iph} in Eq. (3) by H_{int} in Eq. (46), and then applying first-order perturbation theory, we obtain a dispersive pairing interaction of excitons with a van der Waals binding energy of the form

$$U_{bind,el} = (E_{\alpha\beta}/4)(\alpha_{el}/k_o R_{ij}^3)^2. \quad (47)$$

Excitonic van der Waals coupling has already been considered with regard to exciton aggregation.² However, here we will show how this coupling is renormalized by the exciton-phonon interaction.

For this purpose we will first consider a two-site interaction to calculate its contribution from the first-order perturbation theory, and then find its average value. Thus we consider a two-particle electronic state $|F_{ij}\rangle = |F_i\rangle|F_j\rangle$ as the product of two single-particle states, one for each of the two coupled oscillators i and j , respectively. The first-order contribution averaged over all paired sites can be written as

$$\langle H_{int} \rangle = \frac{1}{2} \sum_{i \neq j, \alpha \neq \beta} \langle F_{ij} | H_{int} | F_{ij} \rangle, \quad (48)$$

where the states $|F_i\rangle$ and $|F_j\rangle$ are the unperturbed eigenfunctions of the lower branch $|AD-Q\rangle$ given in Eq. (5). Regrouping the terms in i and j and comparing them with those in Eq. (16) or (13), we obtain

$$\langle H_{int} \rangle = - \sum_{i \neq j, \alpha \neq \beta} \mathbf{p}_{i\alpha\beta}(Q_i) \cdot \mathbf{p}_{j\alpha\beta}(Q_j) / \kappa R_{ij}^3, \quad (49)$$

where $\mathbf{p}_{i\alpha\beta}(Q_k)$ is the adiabatic off-center dipole at site i . Instead of analyzing the results in detail as in Sec. II here we will only mention it briefly. We first select two exciton sites i and j , and consider a Hamiltonian for the system of two coupled oscillators as

$$H_{vib}(Q_i, Q_j) = H_{vib}(Q_i) + H_{vib}(Q_j) + \langle H_{int} \rangle. \quad (50)$$

The wave function of the zeroth-order vibrational eigenstate is chosen as a product of two $u_g(Q_i \pm Q_{jo})$ linear-combination wave functions localized at i and j .⁷ Following this we form symmetric and antisymmetric combinations of the single-well states for both i and j , and then construct their respective products. Then after some lengthy calculations we obtain the level splitting as

$$\delta E_{vib;ij} = 2\{[\delta E_{vib;ii}]^2 + [2\mathbf{p}_{i\alpha\beta}(Q_i) \cdot \mathbf{p}_{j\beta\alpha}(Q_j)/kR_{ij}^3]^2\}^{1/2}, \quad (51)$$

where $\delta E_{vib;ii}$ is the splitting in the absence of pairing as given in Eq. (27), and the second term is the contribution of the pairing. As described in Sec. II, we expand at small pairing strengths (e.g., large R_{ij}) to obtain the vibronic van der Waals binding energy as:

$$U_{bind,vib} = \frac{1}{16}[\delta E_{vib;ij} - 2\delta E_{vib;ii}] = \frac{1}{8}\delta E_{vib;ii}\{[1 + (2\mathbf{p}_{i\alpha\beta}(Q_{io}) \cdot \mathbf{p}_{j\beta\alpha}(Q_{jo})/kR_{ij}^3\delta E_{vib;ii})^2]^{1/2} - 1\} \approx [\delta E_{vib;ii}/4][\alpha_{vib}/kR_{ij}^3]^2. \quad (52)$$

It should be mentioned here that the effective vibronic well-interchange frequency⁷ is $\hbar\omega_{vib} = (1/2)\delta E_{vib;ii}$. As α_{vib} is much higher than α_{el} , it is obvious from Eqs. (47) and (52) that the vibronic binding energy $U_{bind,vib}$ will also be large. Using Eqs. (47) and (52) we can derive the ratio as

$$U_{bind,vib}/U_{bind,el} = 2 \sinh([2E_{JT}/\hbar\omega][1 - (E_{\alpha\beta}/4E_{JT})^2])[1 + E_{\alpha\beta}/4E_{JT}][1 - (E_{\alpha\beta}/4E_{JT})^2](k_o/k_p)^2, \quad (53)$$

where we used $\kappa_p = (\kappa_o^{-1} - \kappa_s^{-1})^{-1}$. Here again we find that the ratio is exponentially large at $4E_{JT} > E_{\alpha\beta} \gg \hbar\omega$. Thus the binding energy of two excitons into a biexciton is enhanced in a polarizable crystalline medium when $4E_{JT} > E_{\alpha\beta} \gg \hbar\omega$.

V. EXCITONS IN LAYERED MATERIALS

The research interest in layered perovskite oxocuprates has been increasing for some time due to their superconducting behavior at not so low temperatures. While the superconducting mechanism is not yet understood, excitons are believed to play a part as they are known to appear in the optical properties of progenitor copper oxide. On the other hand, some of the conceived mechanisms suggest carrier pairing via the mediation of a highly polarizable partner, such as the apex oxygen in an insulating rocksalt layer out of the conducting copper oxide plane. This suggests an interesting form of electron-hole binding through a polarizable partner. It is to be noted that in the case of the enhanced vibronic polarizability of a partner, the resulting binding energy may be larger than the Coulomb attraction or repulsion within an electron-hole or hole-hole pair, respectively. At the same time, due to the large dielectric constant of layered perovskites, especially the one along the c axis, the Coulomb interactions may recede significantly at relatively large distances from the partner. Therefore, we will next consider an electron-hole binding mediated by a polarizable partner with polarizability such as the one described in Sec. III. We will also confine our discussion to the structural geometry of electron-hole pairs in layered materials. Alternative structures and phase diagrams for the Bose condensation of hole-hole pairs have been discussed earlier.¹⁴ We now consider a unit composed of a pair of an electron and hole and a polarizable partner, which is an ion. The binding energy of such a three-body unit is given by

$$U_b = (1/2)\alpha_{vib}(\mathbf{F}_1 + \mathbf{F}_2) \cdot (\mathbf{F}_1 + \mathbf{F}_2), \quad (54)$$

where \mathbf{F}_i for $i=1$ and 2 is the field produced by the i th carrier at the partner site. We use point-charge electrostatics to set $\mathbf{F}_i = \pm(e/\kappa R_i^3)\mathbf{R}_i$, where \mathbf{R}_i is the separation vector between the i th carrier and partner. The upper sign (+) holds when the carrier at i is a hole, and the lower one (−) when there is an electron at i . In a symmetric pair geometry, $R_1 = R_2 = R$. We assume the polarizability tensor to be isotropic

in the xy plane, setting $\alpha_{xx} = \alpha_{yy}$. Introducing then $F_{iz} = F \cos \theta$, where the z axis is along the interconnecting line of the carriers, from Eq. (53) we obtain

$$U_{b\pm} = (e/\kappa R^2)^2 [1 \pm \cos(\mathbf{R}_1, \mathbf{R}_2)] \times [\alpha_{xx} \sin^2 \theta + \alpha_{zz} \cos^2 \theta], \quad (55)$$

where $(\mathbf{R}_1, \mathbf{R}_2) = \pi - 2\theta$ is the angle between \mathbf{R}_1 and \mathbf{R}_2 . The (+) sign applies when the pair is composed of like charge carriers (electron-electron or hole-hole), and the (−) sign applies when it is composed of unlike charge carriers (electron hole). In order to distinguish the two cases, the latter case will be referred to here as ‘‘partner exciton.’’

Minimizing U_{b+} with respect to θ , we obtain the optimal value of θ as

$$\theta_{opt} = \sin^{-1}[\alpha_{zz}/2(\alpha_{zz} - \alpha_{xx})]^{1/2}, \quad (56)$$

at which U_{b+} is minimum. For a strongly anisotropic material $\alpha_{zz} \gg \alpha_{xx}$, we obtain $\theta_{opt} = \pi/4$ and $(\mathbf{R}_1, \mathbf{R}_2) = \pi/2$, which yield $U_{b+}(\theta_{opt}) = \frac{1}{2}(e/\kappa R^2)[\alpha_{xx} + \alpha_{zz}]$. We also note that $U_{b+} = 0$ at $(\mathbf{R}_1, \mathbf{R}_2) = \pi$ ($\theta = 0$), which implies that two electronic carriers of the same sign may not pair when in neighboring Cu-O planes at diametrically opposite sites relative to the partner.

The partner-exciton binding energy U_{b-} is at its highest amounting to $U_{b-} = 2(e/\kappa R^2)\alpha_{zz}$ at $(\mathbf{R}_1, \mathbf{R}_2) = \pi$ ($\theta = 0$), which is a partner exciton formed by an electron and a hole in neighboring conducting planes, and to $U_{b-} = 0$ at $(\mathbf{R}_1, \mathbf{R}_2) = 0$ ($\theta = \pi/2$), which is a Frenkel exciton formed by an electron and a hole in the same conducting plane. Consequently, partner excitons will most likely form sandwichwise by electrons and holes in neighboring planes at diametrically opposite sites relative to a mediator (apex oxygen) in the intercalated rocksalt layer. The polarizability of apex oxygens, known to be large in layered perovskites, may also be enhanced by the vibronic off-center effect.¹⁴

We can now compare the partner exciton binding energy U_{b-} with the Coulomb energy U_c of the electron-hole pair

$$U_c = e^2/\kappa|\mathbf{R}_1 - \mathbf{R}_2| = (e^2/\kappa R)2^{-1/2}[1 - \cos(\mathbf{R}_1, \mathbf{R}_2)]^{-1/2} \quad (57)$$

to obtain

TABLE I. Exciton polarizabilities and van der Waals energies. Calculated as explained in text using data from Table I (Ref. 7). The nearest-neighbor (nn) $\langle 110 \rangle$ binding energies $U_{b,el}$ and $U_{b,vib}$ are calculated at $R_{ij}=2^{1/2}r_o$ using $\langle \cos(\mathbf{p}, \mathbf{F}) \rangle = 1$. The JT energy is computed as $E_{JT} = G_{sp}^2/2K_{sp}$, where $G_{sp} = 4(e/k_p r_o^3) p_{sp}$ (Ref. 10). The notation $q_o^2 = [2E_{JT}/\hbar\omega][1 - (E_{sp}/4E_{JT})^2]$ is also used.

Host	E_{sp} (eV)	p_{sp} (eÅ)	a_{sp} (Å ³)	r_o (Å)	k_o	k_p	G_{sp} (eV/Å)	U_b nn (meV)
RbBr	0.74339	2.30959	103.186	3.445	2.34	4.51	0.72048	27
KI	0.59299	2.58595	162.167	3.533	2.62	5.39	0.62579	37
Host	$\hbar\omega_{sp}$ (meV)	k_{sp} (eV/Å ²)	E_{JT} (eV)	$\mu =$ $E_{sp}/4E_{JT}$	q_o^2	$\delta\hat{E}_{vibsp}$ (meV)	$\hat{\alpha}_{vibsp}$ (Å ³)	$\hat{U}_{b,vib}$ nn (meV)
RbBr	12	1.38409	0.18752	0.99108	0.555	5.678	240	0.3
KI	9	1.23651	0.15835	0.93620	4.347	0.490	24250	159

$$U_{b-}/U_c = (1/\kappa R^3) 2^{1/2} [1 - \cos(\mathbf{R}_1, \mathbf{R}_2)]^{3/2} \times [\alpha_{xx} \sin^2 \theta + \alpha_{zz} \cos^2 \theta]. \quad (58)$$

It is to be noted that at $(\mathbf{R}_1, \mathbf{R}_2) = \pi$ U_{b-} is maximum, but U_c is minimum, and, at $(\mathbf{R}_1, \mathbf{R}_2) = 0$, U_{b-} is minimum but U_c is maximum. At the optimum binding, $(\mathbf{R}_1, \mathbf{R}_2) = \pi(\theta = 0)$, we obtain

$$U_{b-}/U_c = 4(1/\kappa R^3) \alpha_{zz}, \quad (59)$$

where from $U_{b-}/U_c \gg 1$ at $\alpha_{zz} \gg \kappa R^3/4$. Setting $\kappa = 5$ and $R = 1.8 \text{ \AA}$, data typical for layered perovskites, we estimate $\alpha_{zz} \gg 7.3 \text{ \AA}^3$. For comparison, the unit-cell volume of LaCuO_4 is 10^2 \AA^3 . This demonstrates that when two excitons are close enough through a polarizing partner they can form a biexciton with enhanced binding energy.

Certainly, the eigenvalue spectrum of a three-particle unit composed of an electron, a hole, and a binding partner is not easy to derive, though some numerical calculations have been made of the spectrum of paired holes.¹⁵

VI. DISCUSSION

We have investigated the electrostatic response of PJTE vibronic excitons in a polarizable crystalline nonmetallic medium. To the authors' knowledge, this is the first study to deal with the enhancement in the vibronic polarizability associated with excitons in such a medium. As stated above, pairing of excitons through dipole-dipole coupling has been suggested earlier,¹¹ but the renormalization of polarizabilities due to exciton-phonon coupling has not yet been studied. However, the relevant vibronic enhancement of the polarizability has been suggested as an efficient electron-pairing mechanism for high- T_c superconducting materials.^{16,17} van der Waals forces have also been considered for keeping excitons bound in dimers or higher aggregates.² The present study shows that the electrostatic polarizability may increase as a result of symmetry breaking by off-center displacements.

For providing quantitative estimates, we have calculated polarizabilities, vibronic tunneling splittings, and van der Waals energies, both electronic and vibronic, of two alkali halides, and listed them in Table I. We have found that for most materials considered in Table I, the excitonic polaron bands become narrower beyond the range of any meaningful

off-center flip-flop rates. Accordingly excitons in all but two alkali halides may form permanent vibronic dipoles that may also be too rigid to move, and hence no pairing may occur. The remaining two crystals RbBr and KI have been found to show a relatively mild off-centered behavior. In RbBr crystals, excitons are of large radius (very soft), but in KI excitons are of smaller radius (medium hard). An exciton of small radius is about ten times less mobile, though much more polarizable because of a narrower excitonic polaron band. As a result, it pairs vibronically five times more efficiently than does its purely electronic counterpart. However, an exciton of larger radius does not benefit at all from the vibronic coupling. Therefore, the polarizability and mobility do not go together hand in hand in these crystals. In any event, the possibility that a vibronic effect may occur should always be checked while considering the electrostatic response of excited configurational clusters.

An exciton-phonon interaction giving rise to an off-center relaxation has been observed in both highly ionic crystals, such as alkali halides, and in less ionic crystals such as alpha quartz. In all known cases, the coupling originates from the electrostatic interaction and is believed to maintain the local charge neutrality. However, there are impurity centers in ionic crystals with permanent dipole moments, such as OH^- molecular ions, which do not incite any sizable charge-compensating rearrangements on the neighboring ions. Nevertheless, as stated above, our off-center excitons are neutral but polarizable. The nearest-neighbor F-H pair, which is usually referred to as an off-center exciton, consists of two neutral entities, and therefore may not be considered quite similar to the pseudo-Jahn-Teller-type case considered here. It should be stressed that a pseudo-Jahn-Teller argument very similar to ours, although allowing larger anharmonic displacements, has been used for predicting the character of off-center excitons in alkali halides.¹⁸ In fact, in order to take into account the compensating electrostatic effects of the incipient anion vacancy and the trapped hole being displaced toward an interstitial site, the dipole moments calculated in this paper should be multiplied by $[1 - (d_o/r_a)]$, where d_o is the off-center displacement and r_a is the anion vacancy radius. Undoubtedly, the vacancy screening would lower the vibronic pairing energies in a purely ionic crystal, from some 10% to the extent of full extinction. It is to be noted that the vacancy screening effect is not taken into account in Table I.

However, it would be a very desirable exercise indeed to calculate the polarizability of a nearest-neighbor F-H pair coupled with its environment, and compare it with the present results.

Finally, electrons and holes appear simultaneously in layered oxocuprates during photoinduced experiments. After the photoexcitation, holes remain in the oxygen sublattice of the Cu-O plane, whereas electrons are believed to be ultimately trapped at the oxygen vacancies. Excitons in layered materials may therefore be expected to be formed at the initial stages of photoexcitation before the electrons are trapped. Although these stages have so far been investigated less comprehensively, it is believed that future experiments can provide a deeper insight into the fate of photoelectrons, and thus of the mechanism of photoinduced superconductivity.

It should be noted that the behavior of layered perovskites along the c axis is dominated by ionic features. The partner exciton introduced above may be regarded as a form of bound exciton in which the binding energy to a partner ex-

ceeds the electron-hole Coulomb energy. Future studies of partner excitons may disclose whether these are itinerant in layered materials.

The present localized picture is expected to be adequate for dealing with the pairing of self-trapped excitons into biexcitons. It is also adequate to deal with the problem of exciton formation through electron-hole pairing mediated by a partner at the initial stages of the photoexcitation in the parent insulating phase. However, the itinerancy of photoelectrons and photoholes is also essential to take into account, and it is not considered here. Such a problem will be considered in a subsequent study.

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¹J. A. Wheeler, Ann. (N.Y.) Acad. Sci. **48**, 221 (1946).

²M. L. W. Thewalt, in *Excitons*, edited by M. D. Sturge and E. I. Rashba (North Holland, Amsterdam, 1982).

³R. C. Miller, D. A. Kleinman, A. C. Gossard, and O. Munteanu, Phys. Rev. B **25**, 6545 (1982).

⁴D. Birkedal, J. Singh, V. G. Lyssenko, J. Erland, and J. M. Hvam, Phys. Rev. Lett. **76**, 672 (1996).

⁵D. A. Kleinman, Phys. Rev. B **28**, 871 (1983).

⁶J. Singh, D. Birkedal, V. G. Lyssenko, J. Erland, and J. M. Hvam, Phys. Rev. B **53**, 15 909 (1996).

⁷M. Georgiev and J. Singh, Chem. Phys. **176**, 47 (1993).

⁸T. Holstein, Ann. Phys. (N.Y.) **8**, 343 (1959).

⁹I. B. Bersuker, *The Jahn-Teller Effect and Vibronic Interactions*

in *Modern Chemistry* (Plenum, New York, 1984).

¹⁰M. Borissov and M. Georgiev, Z. Phys. B **70**, 413 (1988).

¹¹J. Singh, N. Itoh, and V. V. Truong, Appl. Phys. A: Solids Surf. **49**, 631 (1989).

¹²J. Singh, *Excitation Energy Transfer Processes in Condensed Matter: Theory and Applications* (Plenum, New York, 1994).

¹³H. Haken, *Quantenfeldtheorie des Festkoerpers* (Teubner, Stuttgart, 1973).

¹⁴L. Mihailov, M. Dimitrova-Ivanovich, and M. Georgiev, Physica C **223**, 249 (1994).

¹⁵J. Callaway, D. G. Canhere and P. K. Misra, Phys. Rev. B **36**, 7141 (1987).

¹⁶M. Georgiev and M. Borissov, Phys. Rev. B **39**, 11 624 (1989).

¹⁷M. Borissov and M. Georgiev, Philos. Mag. B **60**, 293 (1989).

¹⁸S. Dzhumanov, Sov. Phys. Solid State **29**, 929 (1987).