PHYSICAL REVIEW B VOLUME 18, NUMBER 12 15 DECEMBER 1978

Pollmann-Büttner variational method for excitonic polarons

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(Received 9 June 1978)

We extend the variational method of Pollmann and Büttner for the effect of polar lattice coupling on effective-mass excitons. Their results correspond to a correction of the dielectric constant; we have added the correction for the polaron mass. We find the polaron mass is strongly quenched to nearly the bare-mass value. We give an analytic result for the case of equal hole and electron masses, and present tabular functions enabling easy binding-energy determinations for any parameter values. Exciton and donor binding energies for specific I-VII and II-VI compounds are given. For the I-VII compounds, donor binding energies are *less* than exciton binding energies. The stronger screening of the heavy ion apparently overwhelms the heavier reduced mass of the donor.

I. INTRODUCTION AND CONCLUSIONS

There is a substantial literature on the problem of the interaction of excitons with virtual phonons, what may be called the excitonic-polaron problem. Much of this work uses perturbation-theoretic methods which have not been numerically trustworthy in the range of interest for excitons in highly polar materials such as II-VI and I-VII semiconductors.

A significant advance was made by Pollmann and Büttner[1] who introduced a method patterned after the intermediate-coupling scheme of Lee, Low, and Pines[2] designed to treat the electronic polaron, i.e., the conventional polaron problem. This method has the advantage of being completely variational and is applicable for the whole range of parameters characterizing the exciton-polaron coupling (except possibly for very strong coupling as might be present in some alkali halides). The method is based on the effective-mass approximation for the bare exciton so the results would not apply to alkali-halide excitons in any case. Comparison with experiment indicates that the variational results are quite good.[3]

In this paper we extend the work of Pollmann and Büttner (PB hereafter) in a number of ways. PB have used s-like trial functions for the phonon displacements. In the weak-coupling limit (exciton binding energy small compared to the optical-phonon frequency) their result leads to an effective exciton Hamiltonian where the Coulomb interaction is screened by the dc dielectric constant ϵ_0, but the kinetic energy is given by the bare-electron and hole masses. We have added p-like terms to the phonon displacements which we can show lead to the correctly renormalized polaron masses in the weak-coupling limit. For the applications to actual materials made so far the improvement in binding energy is less than 10%. (Weak-coupling excitons are normally present only in materials where the electronic-polaron coupling is also weak.)

We have succeeded in obtaining an analytical expression for the excitonic-polaron energy in the case of equal electron and hole masses. For other mass ratios our results are in the form of a one-dimensional integral which must be evaluated numerically as for PB. This integral is a function of two parameters which depend on the electron-hole mass ratio and the optical-phonon energy in units of the bare-exciton binding energy. We present tabular data for the complete range of these two parameters which allows a very quick and simple determination of the 1s exciton binding energy for any material parameters. The third parameter of the problem, the ratio of low- and high-frequency dielectric constants enters in a mathematically trivial way. PB have also calculated exciton binding energies for several cases of interest but their published work does not yield results easily for arbitrary parameters. We find agreement with their results for specific materials. Our improved variational form increases the binding energy by less than 10% in the cases calculated so far. This surprisingly small effect is due to a strong quenching of the mass correction by the exciton binding energy.

We also compute the donor binding energies. For the I-VII compounds the donor binding energies are *smaller* than the exciton binding energies. We attribute this to a strong screening of the positive ion which overwhelms the effect of the greater reduced mass of the donor.

In Sec. II we describe the calculation in detail. In Sec. III we summarize our results, give some specific examples, and some discussion.

II. CALCULATIONAL DETAILS

We follow the method of Pollmann and Büttner[1] almost completely up to the point where we generalize to a more accurate variational form. We summarize some essential steps of their derivation for completeness and for development of notation.

We begin with the Hamiltonian

$$H=\frac{P^2}{2M}+\frac{p^2}{2\mu}-\frac{e^2}{\epsilon_\infty r}+\sum_{\vec{k}}\hbar\omega_L a_{\vec{k}}^\dagger a_{\vec{k}}+\sum_{\vec{k}}V_{\vec{k}}\rho_{\vec{k}}(\vec{r})a_{\vec{k}}e^{i\vec{k}\cdot\vec{R}}+\text{H.c.}\,, \tag{1}$$

$$\rho_{\vec{k}}(\vec{r})=e^{iS_2\vec{k}\cdot\vec{r}}-e^{-iS_1\vec{k}\cdot\vec{r}}, \tag{2}$$

$$V_k=-i(2\pi e^2\hbar\omega_L/v\epsilon^*)^{1/2}/k\,, \tag{3}$$

$$S_i=m_i/M;\quad M=m_1+m_2;\quad \mu=m_1m_2/M\,, \tag{4}$$

$$1/\epsilon^*=1/\epsilon_\infty-1/\epsilon_0\,. \tag{5}$$

ω_L is the longitudinal-phonon frequency, m_1 and m_2 the electron and hole masses, respectively. $\vec{R}, \vec{P}, M$ refer to the center-of-mass variables while $\vec{r}, \vec{p}, \mu$ refer to the relative coordinates. In terms of electron-hole coordinates $\vec{r}_1, \vec{r}_2$, we have

$$\rho_{\vec{k}}(\vec{r})\,e^{i\vec{k}\cdot\vec{R}}=e^{i\vec{k}\cdot\vec{r}_1}-e^{i\vec{k}\cdot\vec{r}_2}\,, \tag{6}$$

which reflects the opposite sign of the electron and hole charges.

We consider an exciton whose center-of-mass momentum is zero and take as our variational wave function

$$|\psi\rangle=U_1U_2|\phi(\vec{r})\rangle\,, \tag{7}$$

$$U_2=\exp\left(\sum_{\vec{k}}f_{\vec{k}}^*(\vec{r})a_{\vec{k}}-f_{\vec{k}}(\vec{r})a_{\vec{k}}^\dagger\right), \tag{8}$$

$$U_1=\exp\left(-i\sum_{\vec{k}}\vec{k}a_{\vec{k}}^\dagger a_{\vec{k}}\cdot\vec{R}\right). \tag{9}$$

$|\phi(\vec{r})\rangle$ is the phonon vacuum with the exciton in a bound state $\phi(\vec{r})$. U_2 displaces each phonon mode linearly in a manner which depends on the relative coordinate $\vec{r}$ while U_1 accounts for the dependence on $\vec{R}$ through the total exciton momentum $-\sum_{\vec{k}}\vec{k}a_{\vec{k}}^\dagger a_{\vec{k}}$.

The energy E is then given by

$$E=\langle\psi|H|\psi\rangle=\langle\phi(\vec{r})|\hbar\omega_LF+E_V+\frac{\vec{K}\cdot\vec{K}+T}{2M}+\frac{(\vec{p}+\vec{j})\cdot(\vec{p}+\vec{j})+G}{2\mu}-\frac{e^2}{\epsilon_\infty r}|\phi(\vec{r})\rangle\,; \tag{10}$$

$$F\equiv\sum_{\vec{k}}f_{\vec{k}}^*f_{\vec{k}};\quad T\equiv\sum_{\vec{k}}\hbar^2k^2f_{\vec{k}}^*f_{\vec{k}}\,;$$

$$G\equiv\hbar^2\sum_{\vec{k}}\vec{\nabla}f_{\vec{k}}^*\cdot\vec{\nabla}f_{\vec{k}};\quad \vec{K}\equiv\sum_{\vec{k}}\hbar\vec{k}f_{\vec{k}}^*f_{\vec{k}}\,;$$

$$\vec{j}\equiv\frac{i\hbar}{2}\sum_{\vec{k}}(f_{\vec{k}}\vec{\nabla}f_{\vec{k}}^*-f_{\vec{k}}^*\vec{\nabla}f_{\vec{k}})\,; \tag{11}$$

$$E_V=-\sum_{\vec{k}}V_k\rho_{\vec{k}}(\vec{r})f_{\vec{k}}+\text{c.c.}\,. \tag{12}$$

We assume $\phi(\vec{r})$ to be real. Then an integration by parts establishes that

$$\langle\phi|\vec{p}\cdot\vec{j}+\vec{j}\cdot\vec{p}|\phi\rangle=0\,. \tag{13}$$

To terms quadratic in $f_{\vec{k}}$ (denoted by E_Q) we have

$$E_Q=\langle\phi(\vec{r})|\hbar\omega_LF+E_V+\frac{T}{2M}+\frac{p^2+G}{2\mu}-\frac{e^2}{\epsilon_\infty r}|\phi(\vec{r})\rangle\,. \tag{14}$$

Pollmann and Büttner have used the s-like variational functions

$$f_{\vec{k}}^s(\vec{r})=(V_k^*/\hbar\omega_L)(\sigma_1e^{-iS_2\vec{k}\cdot\vec{r}}-\sigma_2e^{+iS_1\vec{k}\cdot\vec{r}})\,. \tag{15}$$

We have taken a more general form,

$$f_{\vec{k}}^T(\vec{r})=(V_k^*/\hbar\omega_L)(\tau_1e^{-iS_2\vec{k}\cdot\vec{r}}-\tau_2^*e^{iS_1\vec{k}\cdot\vec{r}})\,, \tag{16}$$

where

$$\tau_n=\sigma_n(1+\lambda_n iq);\quad n=1,2\,, \tag{17}$$

$$q=(\vec{k}\cdot\vec{r})/r\,, \tag{18}$$

and σ_n, λ_n are real and independent of $\vec{r}$.

With these variational functions the expectation value of the energy can be written

$$E_Q=\sum_{\vec{k}}\frac{|V_k|^2}{\hbar\omega_L}(E_k^A+E_k^B)-\frac{e^2}{\epsilon_\infty}\langle r^{-1}\rangle+\frac{\langle p^2\rangle}{2\mu}\,, \tag{19}$$

$$E_k^A=\sigma_1A_1+\sigma_2A_2+\sigma_1^2A_{11}+\sigma_2^2A_{22}+2\sigma_1\sigma_2A_{12}\,, \tag{20}$$

$$E_k^B=\lambda_1B_1+\lambda_2B_2+\lambda_1^2B_{11}+\lambda_2^2B_{22}+2\lambda_1\lambda_2B_{12}\,, \tag{21}$$

$$A_n=2(1-R_{00})\,,$$

$$A_{nn}=1+\hbar^2k^2/2m_n\hbar\omega_L\,,$$

$$A_{12}=-R_{00}\,; \tag{22}$$

$$B_n=2\sigma_nkR_{10}-\tfrac{2}{3}\sigma_n^2\hbar^2k^2\langle r^{-1}\rangle/m_n\hbar\omega_L+\sigma_1\sigma_2\left(\frac{-\hbar^2k^2}{m_{\tilde{n}}\hbar\omega_L}(R_{21}+R_{01})+2kR_{10}\right), \tag{23}$$

$$B_{nn}=\sigma_n^2\frac{k^2}{3}\left(1+\frac{\hbar^2k^2}{2m_n\hbar\omega_L}+\frac{\hbar^2\langle r^{-2}\rangle}{\mu\hbar\omega_L}\right), \tag{24}$$

$$B_{12}=\frac{\sigma_1\sigma_2k^2}{2}\left(\frac{\hbar^2(R_{02}+R_{22}+kR_{11}+kR_{31})-2R_{20}}{\mu\hbar\omega_L}\right), \tag{25}$$

$$\tilde{n}\equiv\tilde{1}=2,\tilde{2}=1\,; \tag{26}$$

$$\langle f(r)\rangle\equiv\int\phi_2(r)f(r)\,d\vec{r}\,, \tag{27}$$

$$R_{nm} \equiv i^n k^{-n} \int \phi^2(r) e^{i\vec{k}\cdot\vec{r}} q^n r^{-m} d\vec{r}\,. \tag{28}$$

E_k^A is the energy obtained from the variational form in Eq. (15) as used by Pollmann and Büttner. E_k^B is the energy resulting from the additional term in Eq. (17).

The variational parameters σ_n, λ_n are easily determined by minimizing E_k^A, E_k^B, respectively, via the general formula

$$\sigma_n^{\min} = (A_{12}A_{\tilde{n}} - A_{\tilde{n}\tilde{n}}A_n)/2D\,, \tag{29}$$

$$D = A_{11}A_{22} - A_{12}^2\,, \tag{30}$$

$$E^A_{k\,\min} = (2A_1A_2A_{12} - A_{11}A_2^2 - A_{22}A_1^2)/4D\,, \tag{31}$$

with an exactly analogous formula for $\lambda_n^{\min}, E^B_{k\,\min}$. Since the B_{ij} depend on the σ_i it is assumed that the σ_i are determined first.

As the simplest reasonable approximation we follow PB in taking for $\phi(r)$ the 1s hydrogenic function

$$\phi(r) = \beta^{3/2}\pi^{-1/2}e^{-\beta r} \tag{32}$$

with β as a further variational parameter chosen to minimize the total energy. With this choice the averages in Eqs. (22)–(28) have the following values

$$\langle r^n \rangle = (n+2)!\,2^{-(n+1)}\beta^{-n}\,, \tag{33}$$

$$\langle p^2 \rangle = \hbar^2\beta^2\,, \tag{34}$$

$$R_{nm} = 2^{m-1}\beta^m G_{n,1-(n+m),2-m}(x)\,, \tag{35}$$

$$G_{n\mu\lambda}(x) = \frac{d^\lambda}{dx^\lambda}\left(x^\mu \tan^{-1}x + \sum_{\substack{\nu=1\\ \nu\ \text{odd}}}^{n} (-1)^{(\nu+1)/2}\frac{x^{\nu+\mu}}{\nu}\right),$$

$$n \geq 0, \quad \lambda \geq 0\,; \tag{36}$$

$$x = k/2\beta\,. \tag{37}$$

With the above relations the following expressions are easily obtained:

$$B_n = -4\beta\left[\sigma_n x^2\gamma + \tfrac{1}{3}\sigma_n^2 x^2\eta_n + \sigma_1\sigma_2(\eta_{\tilde{n}}\delta + x^2\gamma)\right]\,, \tag{38}$$

$$B_{nn} = \tfrac{4}{3}\beta^2\sigma_n^2 x^2(1 + \eta_1 + \eta_2 + \eta_n x^2)\,, \tag{39}$$

$$B_{12} = 4\beta^2\sigma_1\sigma_2[\delta - \gamma x^4 + (\eta_1 + \eta_2)\delta]\,, \tag{40}$$

$$R_{00} = \gamma \equiv (1 + x^2)^{-2}; \quad \delta \equiv 1 - x^{-1}\tan^{-1}x\,, \tag{41}$$

$$\eta_n = 2\hbar^2\beta^2/m_n\hbar\omega_L\,. \tag{42}$$

With the help of these results we can now obtain an expression for the exciton binding energy relative to free polarons

$$E_{\text{BE}} = E_Q - E_{1\,\text{pol}} - E_{2\,\text{pol}} = E^A + E^B - e^2\beta/\epsilon_\infty + \hbar^2\beta^2/2\mu\,, \tag{43}$$

$$E^A = \beta C\int_0^\infty (E^A_{k\,\min} + A_{11}^{-1} + A_{22}^{-1})dx\,,$$

$$E^B = \beta C\int_0^\infty E^B_{k\,\min}\,dx\,, \tag{44}$$

$$C = (2e^2/\pi)(1/\epsilon_\infty - 1/\epsilon_0)\,. \tag{45}$$

The free polaron energy of the electron $E_{1\,\text{pol}}$ is accounted for by the term A_{11}^{-1} in the integrand in Eq. (44).

By maximizing the value of E_{BE} as a function of β we then obtain our final variational expressions for the binding energy[4]

$$E_{\text{BE}} = -|E_\infty|G_1G_2\,, \tag{46}$$

$$G_n = 1 - (1 - \epsilon_\infty/\epsilon_0)F_n\,, \tag{47}$$

$$F_1 = (2/\pi)F_d\,; \quad F_2 = (2/\pi)(2F - F_d)\,, \tag{48}$$

$$F_d = F + 2\left(\eta_1\frac{\partial F}{\partial\eta_1} + \eta_2\frac{\partial F}{\partial\eta_2}\right), \tag{49}$$

$$F = \int_0^\infty (E^A_{k\,\min} + A_{11}^{-1} + A_{22}^{-1} + E^B_{k\,\min})dx\,, \tag{50}$$

$$\beta = \beta_\infty G_1; \quad \eta_n = 2\hbar^2\beta_\infty^2 G_1^2/m_n\hbar\omega_L\,, \tag{51}$$

$$\beta_\infty = e^2\mu/\hbar^2\epsilon_\infty, \quad |E_\infty| = e^4\mu/2\hbar^2\epsilon_\infty^2\,. \tag{52}$$

Since F_1, F_2 depend on the parameters η_1, η_2 which are defined by Eq. (51), the equations must be solved self-consistently for η_1, η_2. The numerical values of $F_1(\eta_1, \eta_2), F_2(\eta_1, \eta_2)$ are given in Table I. The variation with η is slow hence it is relatively easy to obtain self-consistent results starting with $\beta = \beta_\infty$, for example.

It is instructive to supplement the results in Table I by analytical expressions which can be obtained for various limiting cases. We concentrate first on the energy E_A, which will be seen to give the major contribution to the binding energy. For the case of equal bare masses ($m_1 = m_2$) we can perform the integral over x in Eq. (44) and obtain the result

$$E^A = \beta C\left\{\frac{\pi}{2} + \frac{\pi}{\sqrt{\eta}} - \frac{\pi\eta}{(1-4\eta)^{1/2}}[(1+r_1)(1-r_1)^{1/2} - (1+r_2)(1-r_2)^{1/2}]\right\}, \tag{53}$$

$$r_1 + r_2 = -1/\eta; \quad r_1r_2 = 1/\eta; \quad \eta = 2\hbar^2\beta^2/m\hbar\omega_L\,; \tag{54}$$

$$r_n = [-1 + s_n(1-4\eta)^{1/2}]/2\eta\,; \quad s_1 = 1, \ s_2 = -1;$$
$$m_1 = m_2 = m\,. \tag{55}$$

The roots r_n yield the poles of the integrand. Even for unequal masses the integral can be expressed in terms of contributions from the poles of the integrand but in this case the roots of a high-order polynomial must be found. Equation (53) is still not too illuminating so we consider further limiting cases:

$$E^A = \beta C\left(\frac{\pi}{2} - \frac{\pi}{2}\eta^{3/2} + \cdots\right) \ \text{small}\ \eta, \quad m_1 = m_2\,; \tag{56}$$

$$E^A = \beta C\left(\frac{\pi}{\sqrt{\eta}} - \frac{13\pi}{16\eta} + \cdots\right) \ \text{large}\ \eta, \quad m_1 = m_2\,. \tag{57}$$

TABLE I. The tabulated functions F_1,F_2 yield the ground-state exciton binding energy via Eqs. (46) and (47) together with a self-consistent determination of the parameter η_1 via Eq. (51).

	$F_1(\eta_1, \eta_2)$; $\eta_2 = \eta_1 m_1/m_2$							
	Mass ratio $m_1/m_2 \rightarrow$							
$\log_{10}\eta_1$	1.0	0.8	0.6	0.4	0.2	0.1	0.05	0.0
−2.0	0.98146	0.98259	0.98388	0.98542	0.98743	0.98883	0.98973	0.99177
−1.8	0.97572	0.97726	0.97902	0.98113	0.98387	0.98578	0.98707	0.98972
−1.6	0.96790	0.97001	0.97245	0.97539	0.97922	0.98186	0.98366	0.98722
−1.4	0.95713	0.96007	0.96348	0.96763	0.97307	0.97682	0.97934	0.98420
−1.2	0.94217	0.94628	0.95111	0.95702	0.96486	0.97028	0.97389	0.98062
−1.0	0.92112	0.92695	0.93383	0.94232	0.95371	0.96166	0.96694	0.97640
−0.8	0.89117	0.89950	0.90936	0.92161	0.93825	0.94999	0.95782	0.97134
−0.6	0.84850	0.86032	0.87439	0.89201	0.91626	0.93363	0.94532	0.96499
−0.4	0.78896	0.80523	0.82481	0.84964	0.88448	0.91001	0.92748	0.95654
−0.2	0.70991	0.73101	0.75688	0.79043	0.83892	0.87565	0.90147	0.94483
0.0	0.61256	0.63776	0.66946	0.71190	0.77594	0.82679	0.86395	0.92856
0.2	0.50335	0.53064	0.56608	0.61545	0.69421	0.76071	0.81189	0.90670
0.4	0.39268	0.41935	0.45520	0.50745	0.59648	0.67745	0.74391	0.87906
0.6	0.29140	0.31499	0.34785	0.39806	0.49000	0.58100	0.66152	0.84691
0.8	0.20696	0.22606	0.25360	0.29767	0.38460	0.47875	0.56938	0.81320
1.0	0.14186	0.15627	0.17767	0.21343	0.28927	0.37927	0.47402	0.78150
1.2	0.09469	0.10497	0.12064	0.14787	0.20958	0.28960	0.38189	0.75459
1.4	0.06201	0.06906	0.08005	0.09975	0.14716	0.21387	0.29798	0.73362
1.6	0.04009	0.04479	0.05225	0.06598	0.10072	0.15333	0.22539	0.71834
1.8	0.02570	0.02877	0.03372	0.04302	0.06755	0.10709	0.16548	0.70771
2.0	0.01638	0.01837	0.02159	0.02776	0.04458	0.07313	0.11815	0.70058

	$F_2(\eta_1, \eta_2)$; $\eta_2 = \eta_1 m_1/m_2$							
	Mass ratio $m_1/m_1 \rightarrow$							
$\log_{10}\eta_1$	1.0	0.8	0.6	0.4	0.2	0.1	0.05	0.0
−2.0	1.00083	1.00072	1.00059	1.00043	1.00020	1.00001	0.99991	0.99995
−1.8	1.00142	1.00124	1.00103	1.00076	1.00041	1.00013	0.99993	0.99989
−1.6	1.00237	1.00208	1.00174	1.00130	1.00071	1.00030	1.00000	0.99979
−1.4	1.00386	1.00342	1.00287	1.00216	1.00118	1.00051	1.00006	0.99959
−1.2	1.00619	1.00550	1.00464	1.00351	1.00194	1.00084	1.00013	0.99926
−1.0	1.00983	1.00875	1.00742	1.00568	1.00320	1.00142	1.00027	0.99877
−0.8	1.01550	1.01385	1.01182	1.00918	1.00537	1.00255	1.00068	0.99819
−0.6	1.02400	1.02161	1.01868	1.01481	1.00913	1.00481	1.00183	0.99771
−0.4	1.03537	1.03238	1.02857	1.02339	1.01542	1.00905	1.00447	0.99771
−0.2	1.04754	1.04471	1.04075	1.03486	1.02487	1.01614	1.00943	0.99860
0.0	1.05520	1.05413	1.05176	1.04701	1.03679	1.02622	1.01719	1.00051
0.2	1.05030	1.05307	1.05486	1.05448	1.04805	1.03778	1.02715	1.00310
0.4	1.02469	1.03309	1.04160	1.04935	1.05258	1.04681	1.03688	1.00521
0.6	0.97387	0.98852	1.00512	1.02379	1.04264	1.04705	1.04185	1.00465
0.8	0.89927	0.91931	0.94349	0.97358	1.01166	1.03165	1.03632	0.99871
1.0	0.80741	0.83095	0.86065	0.90019	0.95720	0.99594	1.01526	0.98536
1.2	0.70707	0.73194	0.76441	0.80987	0.88191	0.93920	0.97619	0.96440
1.4	0.60639	0.63077	0.66343	0.71100	0.79214	0.86463	0.91961	0.93753
1.6	0.51136	0.53399	0.56493	0.61142	0.69550	0.77789	0.84842	0.90744
1.8	0.42554	0.44574	0.47380	0.51698	0.59886	0.68534	0.76696	0.87676
2.0	0.35049	0.36801	0.39264	0.43128	0.50734	0.59274	0.68006	0.84750

These results lead to the values

$$F_1^A = 1 - 4\eta^{3/2}; \quad F_2^A = 1 + 2\eta^{3/2}; \quad \text{small } \eta, \quad m_1 = m_2 \tag{58}$$

$$F_1^A = \frac{13}{8\eta}; \quad F_2^A = \frac{4}{\sqrt{\eta}} - \frac{39}{8\eta}; \quad \text{large } \eta, \quad m_1 = m_2 \tag{59}$$

for the E^A contribution to the tabulated functions

F_1, F_2.

In the limit of $m_2 = \infty$ the expressions do not simplify appreciably, hence we have not found a general analytical formula in this case. It is relatively easy to find leading terms in an expansion in η (η^{-1}) in the limit of small (large) η.

$$F_1^A = \tfrac{11}{16}; \quad F_2^A = 2\eta^{-1/2} + \tfrac{11}{16}; \quad \eta \gg 1, \quad m_2 = \infty . \tag{60}$$

The asymptotic expression given by PB [Eq. (C5) in Appendix C] corresponds to $F_1^A = F_2^A = \frac{11}{16}$.

For small η we find

$$F_1^A = F_2^A = 1 + O(\eta^{3/2}); \quad \eta \ll 1, \quad m_2 = \infty . \tag{61}$$

We also wish to demonstrate that in the limit of small η (weak exciton binding) the variational form we have assumed leads to exciton binding energies based on polaron masses rather than bare masses. We need to evaluate the energy E^B in Eq. (44) from Eq. (31) with A substituted by B as given in Eqs. (38)–(42). We note that for the case of $\eta = 0$ the integral does not converge, hence for very small η, E^B is determined by very large values of x. In this limit γ, $\delta \to 0$ and we can write

$$\begin{aligned} B_n &= -\tfrac{4}{3}\beta\sigma_n^2 x^2 \eta_n , \\ B_{nn} &= \tfrac{4}{3}\beta^2\sigma_n^2 x^2 (1 + \eta_n x^2) , \\ B_{12} &= 0; \quad \sigma_n = -1/(1 + \eta_n x^2); \end{aligned} \tag{62}$$

$$\begin{aligned} E^B &= \beta C \int_0^\infty \left(-\frac{B_1^2}{4B_{11}} - \frac{B_2^2}{4B_{22}} \right) dx \\ &= -\frac{\hbar^2\beta^2}{12}\left(\frac{\alpha_1}{m_1} + \frac{\alpha_2}{m_2} \right), \end{aligned} \tag{63}$$

$$\alpha_n = \frac{e^2}{\hbar}\left(\frac{m_n}{2\hbar\omega_L} \right)^{1/2} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right), \tag{64}$$

where α_n is the polaron coupling constant for particle n. Using this value for E^B in Eq. (43) we see that the bare masses m_n are replaced by

$$m_n^{**} = m_n / (1 - \tfrac{1}{6}\alpha_n) . \tag{65}$$

A more accurate expression[2] for m_n^{**} is $m_n(1 + \frac{1}{6}\alpha_n)$. We have obtained the perturbation theory result because we have limited ourselves to terms quadratic in the phonon displacements in Eq. (14).

We may also note that the approximation $E^A = \beta C\pi/2$ in Eq. (56) has the effect of altering the effective dielectric constant from ϵ_∞ to ϵ_0 in the small exciton binding limit as already noted by PB. Thus our variational result renormalizes the ϵ_∞ and m_n parameters in two stages corresponding to the energies E^A and E^B to give ϵ_0 and m_n^{**} which is the result one would intuitively expect for weakly bound polarons.

III. SUMMARY AND DISCUSSION

We have followed Pollmann and Büttner[1] in taking a variational wave function for the excitonic polaron patterned after the classic paper of Lee, Low, and Pines.[2] The wave function is given in Eqs. (7)–(9) with $\phi(\vec{r})$ taken as a 1s hydrogenic wave function in the numerical work. Taking the Hamiltonian to second order in the phonon displacements $f_{\vec{k}}(\vec{r})$ leads to the energy expression in Eq. (14).

PB[1] have used "s-" like displacements of the phonon coordinates σ_1, σ_2 in Eq. (15) which lead to variational energies we have called E^A. We have extended their work by adding "p-" like terms $\lambda\vec{k}\cdot\vec{r}/r$ as in Eq. (17) giving an energy E^B.

In the limit of exciton binding energy small compared to the phonon energy, the energy E^A serves to renormalize the effective dielectric constant from the value ϵ_∞ in the unperturbed problem to the value ϵ_0. Similarly, the energy E^B acts to renormalize the bare masses m_1, m_2 to the polaron masses m_1^{**}, m_2^{**}.

In general, the complete solution to the excitonic polaron ground-state energy is given by Eqs. (46), (47), (51), and (52) in terms of two functions $F_1(\eta_1, \eta_2), F_2(\eta_1, \eta_2)$ which depend on η_1, η_2 in a relatively slow fashion as given in Table I. The solution of the problem is still implicit via the dependence of η_n on F_1, F_2 but in practice it converges rapidly using iteration starting with $G_1 = 1$. Analytic formulas for F_1^A, F_2^A, the contribution to F_n from the energy E^A are given for the case of equal masses in Eqs. (53)–(59) and for various limits with $m_2 = \infty$ in Eqs. (60) and (61).

The functions F_1^A, F_2^A resulting from PB's variational form are compared with the more accurate F_1, F_2 in Table II. The differences appear to be small in spite of the qualitative feature that F_1^A, F_2^A effectively contain bare masses while F_1, F_2 contain polaron masses as demonstrated in Eqs. (62)–(65).

Excitonic binding energies have been computed for several cases of practical interest in Table IIIA. We confirm PB's earlier numerical results and find that our more accurate results only increase the binding energy by a few percent, the maximum increase being 7% for TlBr.

Except for the case of AgBr, the theoretical results agree reasonably well with the experimental numbers. The experimental parameters are too uncertain to allow a good test of the accuracy of the theory. The hole mass m_h is often the most uncertain experimental value. The theory could be used in reverse to determine an effective m_h from the observed exciton binding energy.

Referring to Eq. (43), Pollmann and Büttner's

TABLE II. A shortened version of Table I showing the values of F_1, F_2 (denoted F_1^A, F_2^A) given by the simpler Pollmann–Büttner variational form, Eq. (15).

	$\eta_2=\eta_1$; $m_1=m_2$				$\eta_2=0$; $m_2=0$			
η_1	F_1^A	F_2^A	F_1	F_2	F_1^A	F_2^A	F_1	F_2
0.01	0.997 12	1.001 34	0.981 46	1.000 83	0.999 97	1.000 02	0.991 77	0.999 95
0.1	0.949 96	1.020 20	0.921 12	1.009 83	0.997 89	1.001 16	0.976 40	0.998 77
1.0	0.616 09	1.085 63	0.612 56	1.055 20	0.949 77	1.020 79	0.928 56	1.000 51
10.0	0.139 16	0.817 33	0.141 86	0.807 41	0.777 94	1.007 60	0.781 50	0.985 36
100.0	0.015 98	0.351 70	0.016 38	0.350 49	0.699 40	0.851 24	0.700 58	0.847 50

binding energy $E^{\rm PB}$ is given by

$$E_{\rm BE}^{\rm PB}=E^A-e^2\beta/\epsilon_\infty+\hbar^2\beta^2/2\mu\,. \qquad (66)$$

We may define an effective dielectric function $\epsilon_{\rm eff}$ by

$$E_{\rm BE}^{\rm PB}=(\epsilon_\infty/\epsilon_{\rm eff})^2E_\infty \qquad (67)$$

with E_∞ given by Eq. (52). We may further define an effective polaron mass by the relation

$$E_{\rm BE}=(\mu_{\rm eff}/\mu)E_{\rm BE}^{\rm PB}\,. \qquad (68)$$

These values have been tabulated in Table III B together with their limiting values $\epsilon_0/\epsilon_\infty$ and μ^{**}/μ. From the table it is clear that the dielectric factor $\epsilon_0/\epsilon_\infty$ is much more important than the mass factor μ^{**}/μ since it is always bigger and furthermore enters the binding energy squared, whereas μ^{**}/μ enters linearly. Nevertheless, the mass factor is significant, ranging from 30% to 40% for the halides. When the ratio of phonon energy to bare Coulomb energy $\hbar\omega_L/E_\infty$ is small we expect the phonon contributions to the binding energy to be quenched. The excitonic polarizability tends to zero and $\epsilon_{\rm eff}/\epsilon_\infty$ and $\mu_{\rm eff}/\mu$ should tend to 1.

TABLE III. Exciton and donor binding energies for a number of II–VI and I–VII compounds. Rows marked by an asterisk use parameter values from Beni and Rice (Ref. 5). The other parameters are from Pollmann and Büttner (Ref. 3). m_e, m_h are bare masses renormalized by the polaron coupling constants to $m_e^{**}=m_e(1+\alpha_e/6)$ to give μ^{**}, the renormalized reduced mass. All energies in meV, masses in electron mass units. $\epsilon_{\rm eff}$, $\mu_{\rm eff}$ are effective values of the dielectric constant and polaron reduced mass defined via Eqs. (67) and (68) to give the binding energy via the simple hydrogenic formula.

(A)

	m_e	m_h	ϵ_0	ϵ_∞	ω_L	$E_{\rm xpt}^{\rm exc}$	$E_{\rm th}^{\rm exc}$	$E_{\rm th}^{\rm don}$	
AgBr	0.221	0.70	10.6	4.68	17.3	16.0	49.5	34.8	*
CdS	0.185	1.10	8.58	5.26	36.8	27.0	38.2	37.6	*
	0.18	0.70	9.7	5.2	38.0	29.0	28.9		
CdSe	0.116	0.69	9.4	6.2	26.1	15.0	18.1	19.1	*
CuCl	0.44	3.6	7.4	3.7	27.2	190.0	232.0	147.0	
GaAs	0.07	0.50	13.1	11.1	36.8	4.7	4.95	5.60	
TlBr	0.18	0.38	35.1	5.4	14.3	9.8	8.09	2.82	
TlCl	0.37	0.36	37.6	5.1	21.5	11.8	16.3	5.75	
ZnO	0.24	0.49	8.59	4.0	72.0	59.0	46.7	51.0	*
	0.28	0.59	8.6	4.0	72.0	59.8	58.0		
ZnS	0.25	0.59	8.6	5.2	43.6	36.0	44.8	51.3	*

(B)

	α_e	α_h	$\epsilon_0/\epsilon_\infty$	$\epsilon_{\rm eff}/\epsilon_\infty$	μ^{**}/μ	$\mu_{\rm eff}/\mu$	ω_L/E_∞	
AgBr	1.57	2.80	2.26	1.46	1.306	1.008	0.166	*
CdS	0.608	1.48	1.63	1.44	1.120	1.015	0.473	*
CdSe	0.427	1.04	1.52	1.40	1.085	1.016	0.744	*
CuCl	2.00	5.73	2.00	1.30	1.382	1.003	0.0697	
GaAs	0.070	0.187	1.18	1.18	1.014	1.007	5.43	
TlBr	2.05	2.98	6.50	2.74	1.388	1.068	0.251	
TlCl	2.59	2.56	7.37	2.48	1.429	1.049	0.225	
ZnO	0.899	1.29	2.15	1.74	1.17	1.027	0.526	*
ZnS	0.671	1.03	1.65	1.41	1.13	1.014	0.494	*

It is seen that this quenching effect is considerably stronger for the mass correction. As a result, Pollmann and Büttner's much simpler variational form is a quite good approximation to the cases considered here.

We may note another interesting fact contained in Table IIIA. We have computed both the exciton binding energy and the donor binding energy. We observe that for all the halides the donor binding energy is less than the exciton binding energy. The greater localizability of the heavy particle leads to a more complete screening of its charge by the lattice which appears to outweigh the increase of the reduced mass.

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[1] J. Pollmann and H. Büttner, Phys. Rev. B 16, 4480 (1977).

[2] T. D. Lee, F. E. Low, and D. Pines, Phys. Rev. 90, 297 (1953).

[3] J. Pollmann and H. Büttner, Solid State Commun. 17, 1171 (1975).

[4] We should note that our results are fully variational for the energy E^A. We have limited ourselves to quadratic terms in the phonon displacements in calculating E^B in Eq. (14), hence our results are not variational for strong phonon coupling.

[5] G. Beni and T. M. Rice, Phys. Rev. B 18, 768 (1978).