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Optical spectra of molecular crystals: The effect of exciton band structure on spectra and linewidths

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We discuss the spectrum (linewidths and positions) of the first triplet state of the molecular crystals anthracene, napthalene, and phenazine. These crystals have similar exciton bandwidths, but varying amounts of anisotropy in the intermolecular interactions. We analyze the linewidths at zero temperature using isotopic scattering as the broadening mechanism, and the temperature dependence using one and two phonon scattering processes as the broadening mechanism.

I. INTRODUCTION

Although the static properties of the excited electronic states of molecular crystals (e.g., energy levels and optical spectral intensities) have been studied for a number of years¹ and are reasonably well understood, at least for the low-lying states, the dynamic properties are much less studied or understood. For example, the interaction of phonons with excitons leads to optical line broadening and the temperature dependence of line positions and widths. Although the basic theoretical models for these effects are well studied formally,² there have been few attempts at systematic investigations.³ In the present paper, we examine the optical spectrum (specifically the linewidths for the 0-0 transition) in a series of systems (anthracene, naphthalene, and phenazine) which have similar geometric structures and exciton bandwidths, but different anisotropies of the intermolecular interactions which give rise to the exciton band structure. This difference means that even though the exciton bandwidths are similar in these systems, the detailed structure of the two Davydov components of the band are quite different. This leads to measurable differences in the linewidths and their temperature dependences which can be understood on the basis of a simple model which we present below. From the model, we find the electron-phonon coupling constants for the three systems and assess the importance of impurity and phonon scattering in line broadening. It should be emphasized that this analysis rests on the assumption that the inhomogeneous broadening of spectral lines (due to crystal defects and other impurities) is negligible. This assumption is well borne out in the high quality crystals used in the experiments.

II. RESULTS-EXPERIMENTAL

A. Optical spectra

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The $T_1 \leftarrow S_0$ electronic spectra of anthracene, naphthalene, and phenazine crystals at low T are presented in Fig. 1. The details of the experimental method and crystal preparation can be found in Refs. 2(b) and 4(a).

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The linewidths of the lower and upper component 0-0 in

these three crystals were measured as a function of temperature and these widths expressed as (i = 1 lower component; i = 2 upper component)

$$\Gamma_i = \Gamma_i^{(0)} + \delta \Gamma_i(T) \tag{1}$$

with the temperature-dependent part of the width fit to a form

$$\delta\Gamma_i(T) = G_i[n_E + \delta_{il}] + G_3\Gamma_{\text{RAM}},$$
(2)

where

$$n_E = (e^{\beta E} - 1)^{-1} \tag{3}$$

is the phonon population at energy E. In these equations, δ_{ij} is the Kronecker delta function equal to 1 if the indices are equal and 0 otherwise, $\beta = (kT)^{-1}$, where k is Boltzmann's constant, and the G_i have units of cm⁻¹. The values of G_i as well as other relevant parameters are given in Table I and the fit shown in Fig. 2. The term Γ_{RAM} is the usual Raman or two phonon line shape function

$$\Gamma_{\rm RAM} = \int_0^{T_D/T} \frac{x^6 e^x}{(e^x - 1)^2} dx (T/T_D)^7.$$
 (4)

B. Exciton band structures

Anthracene, naphthalene, and phenazine crystallize in the monoclinic crystal system $(C_{2h}^{5} \text{ or } P2_{1/a})$ with two translationally inequivalent molecules per unit cell. This structure leads to an exciton band structure which has been studied since the classic work of Davydov.¹ For the triplet excitons, the two nearest-neighbor interactions are known to be the largest: the equivalent pair interaction J_{AA} and the inequivalent pair interaction J_{AB} . These have been measured by Port and co-workers in dilute doped crystals and are listed in Table II for these three crystals. The exciton energy levels for this general class of crystals is given by

$$E_i(\mathbf{k}) = E_0 + 2 J_{AA} \cos \mathbf{k} \cdot \mathbf{a} + (-1)^i 4 |J_{AB}| (\cos \mathbf{k} \cdot \mathbf{a}/2)$$
$$\times (\cos \mathbf{k} \cdot \mathbf{b}/2), \quad i = 1, 2, \tag{5}$$

where we have used the fact that there are four translational-

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FIG. 1. The electronic spectrum of $T_1 \leftarrow S_0$ transition in anthracene, naphthalene, and phenazine. The temperature in all three experiments is 1.6 K. The polarization is ||b| for phenazine, and a composite of the ||a| and ||b| polarizations for anthracene and naphthalene. Note that the zero field substructure is evident for phenazine in this polarization. Note also the rather complex structure in the upper Davydov component of naphthalene.

ly inequivalent molecules surrounding any site, one at $\frac{1}{2}(a+b)$, one at $\frac{1}{2}(a-b)$, one at $-\frac{1}{2}(a+b)$, and one at $\frac{1}{2}(-a+b)$. The exciton band structure is plotted vs $|\mathbf{k}|$ for $\mathbf{k}||\mathbf{a}^{-1}$ and \mathbf{b}^{-1} in Figs. 3, 4, and 5 for the three crystals. Note the striking differences, especially between phenazine on one hand and anthracene and naphthalene on the other hand. The anisotropy of the interactions increases from anthracene to naphthalene to phenazine, while the bandwidths (defined as the difference in energy between the highest and lowest energy levels in the band) in anthracene and phenazine are approximately equal and twice that of naphthalene. Thus the anisotropy should play a major role in the *differences* among these three systems, which have similar bandwidths.

In phenazine, Griese⁴ has measured nonnearest-neighbor interactions using optical spectroscopy in isotopically (deuterated) substituted mixed crystals. He finds that, in contrast to anthracene and naphthalene, the nonnearest-neighbor interactions in phenazine are measurable. The bandwidth and band structure can still be fit reasonably well with *effective* nearest-neighbor J_{AA} and J_{AB} values. These are given in parentheses in Table II, next to the measured values of J_{AA} and J_{AB} . In what follows, we use the measured values.

TABLE I. Parameters used in the fit of experimental data to linewidths and temperature dependence given by Eqs. (1) and (2).

	Anthracene	Naphthalene	Phenazine
<i>G</i> ,	$0.5 \pm 0.2 \text{ cm}^{-1}$	0.1 cm ⁻¹	0.025 cm ⁻¹
G_1	$0.8 \pm 0.2 \text{ cm}^{-1}$	0.1 cm^{-1}	$0.010 \mathrm{cm}^{-1}$
Ė	$\sim 20 \text{ cm}^{-1}$	$\sim 9 \text{ cm}^{-1}$	$\sim 3 \text{ cm}^{-1}$
G_3	40 cm^{-1}	100 cm ⁻¹	$70 \mathrm{cm}^{-1}$
TDebve	90 K	100 K	80 K
$\Gamma_1^{(0)}$	$0.009 \mathrm{cm}^{-1}$	0.07 cm ⁻¹	0.0065 cm^{-1}
$\Gamma_2^{(0)}$	$0.4 \pm 0.1 \text{ cm}^{-1}$	0.3 cm^{-1}	0.11 cm^{-1}

III. THEORETICAL ANALYSIS

We expect the spectral linewidths to be given by two effects: (a) phonon scattering (dynamic disorder) which should be temperature dependent; and (b) static disorder, which in good crystals should largely be due to scattering from isotopic disorder.^{3,5}

A. Phonon scattering

In pure crystals, the optical absorption obeys the $\Delta \mathbf{k} \simeq \mathbf{0}$ selection rule. Since the ground state is a $\mathbf{k} = \mathbf{0}$ state, the width of the absorption spectrum is governed by the scattering of the excited states at $\mathbf{k} = 0$. At low T, in systems of this kind, we expect the phonon scattering to be dominated by two mechanisms: (1) one phonon emission or decay; and (2) two phonon Raman processes. The interaction terms responsible for these are^{1,6}

$$V_{1} = \sum_{\substack{k,q,\lambda\\i,j}} F_{1}^{\lambda}(k+q,i;k,j) | k+q;i \rangle \langle k;j | (b_{q\lambda} + b_{-q\lambda}^{+})$$
(6)

and

$$V_{2} = \sum_{\substack{k,q,q',\lambda,\lambda'\\i,j}} F_{2}^{\lambda\lambda'}(k+q+q',i;k_{j})|k+q+q';i\rangle$$
$$\times \langle k;j|(b_{q\lambda}+b_{-q\lambda}^{+})(b_{q'\lambda}+b_{-q\lambda'}^{+}).$$

In these expressions, $|k;i\rangle$ represents an exciton state with wave vector k and i represents the upper (i = 2) or lower (i = 1) component, and $b_{q\lambda}(b_{q\lambda}^+)$ destroys (creates) a phonon of wave vector q and branch (or band) λ . Note that the wave vector is conserved. The parameters $F_1^{\lambda}(k+q,i;k,j)$ and $F_2^{\lambda\lambda'}(k+q+q',i;k,j)$ are excitonphonon interaction terms whose form will be discussed be-

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FIG. 2. The experimental fit of the linewidth [fullwidth at half-maximum (FWHM)] of upper and lower Davydov components in anthracene, naph-thalene, and phenazine crystals.

low. In the present cases, the variations of the linewidths with temperature are dominated (at temperatures up to $\sim 15 \text{ K}$) by the one phonon terms. We will therefore restrict our attention to those processes and parameters.

Using second order perturbation theory (Fermi's Golden rule), we find the rate of scattering from the k = 0 state of the lower (subscript 1) and upper (subscript 2) components to be given for *one phonon* processes by

$$\Gamma_{1}^{(1)}(\mathbf{k}=\mathbf{0}) = \sum_{q,\lambda} |F_{1}^{\lambda}(\mathbf{q},1;\mathbf{0},\mathbf{2})|^{2} \,\overline{n}(\omega_{q\lambda}) \delta(E_{2}(0) + \omega_{q} - E_{1}(\mathbf{q})), \tag{8}$$

$$\Gamma_{2}^{(1)}(\mathbf{k}=\mathbf{0}) = \sum_{q,\bar{\lambda}} |F_{1}^{\lambda}(\mathbf{q},2;\mathbf{0},1)|^{2} [\bar{n}(\omega_{q\lambda}) + 1] \delta(E_{1}(\mathbf{0}) - \omega_{q} - E_{2}(\mathbf{q})).$$
(9)

TABLE II. Intermolecular matrix elements: J_{AA} is the equivalent molecular interaction; J_{AB} is the inequivalent molecule interaction.

	Anthracene	Naphthalene	Phenazine
J	$-2.0 \mathrm{cm^{-1}}$	- 0.57	$-4.5 \text{ cm}^{-1} (-5.6 \text{ cm}^{-1})^{a}$
J_{AB}	-2.5 cm ⁻¹	+ 1.2	$+ 0.4 \text{ cm}^{-1} (0.4 \text{ cm}^{-1})^{a}$

* See the discussion at the end of Sec. II.

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FIG. 3. The triplet exciton band structure for anthracene calculated using the parameters of Table II. Note that the bands ||c - 1| will be flat.

The delta function conserves energy in the process. We have noted that it is impossible to scatter from states in the lower Davydov component to other states in that component by a one phonon process because of wave vector conservation. For the systems under consideration, it is not possible to calculate the $|F_1^{\lambda}|^2$, so we will make a simple deformation potential approximation and take for the acoustic modes

$$|F_{1}^{\lambda}(qi|0j)|^{2} = \frac{\gamma_{ij}^{2}\omega_{q}}{N},$$
(10)

where N is the number of unit cells in the crystal, so that

$$\Gamma_1^{(1)}(\mathbf{k} = \mathbf{0}) \cong 3\gamma_{12}^2 \ \vec{n}(\omega_0) \cdot \omega_0 \rho_{\rm AC}(\omega_0), \tag{11}$$

$$\Gamma_{2}^{(1)}(\mathbf{k} = \mathbf{0}) \cong 3\gamma_{21}^{2}(\bar{n}(\omega_{1}) + 1)\omega_{1}\rho_{AC}(\omega_{1}).$$
(12)

Here, γ_{ij} are unknown matrix elements which will be taken to be a fitting parameter, ω_0 is the energy of the phonon which can be absorbed in taking the system from the k = 0state of the lower DC to the upper while conserving energy and wave vector, and ω_1 is the energy of the phonon which can be created when the exciton goes from the upper $\mathbf{k} = \mathbf{0}$ state to the lower (Davydov component (DC). Of course, ω_0 (or ω_1) is actually an average over a number of such



FIG. 4. The triplet exciton band structure for naphthalene calculated using the parameters of Table II. Note that the bands ||c - 1| will be flat.



FIG. 5. The triplet exciton band structure for phenazine calculated using the parameters of Table II. Note that the bands ||c - 1| will be flat.

frequencies; however, the acoustic branches in these crystals are much more isotropic than the exciton bands, and the phonon bandwidths so much larger than the exciton bandwidths, that this is an average over a narrow frequency range. Therefore, a single value is a good approximation. We see from the exciton band structure that

$$\omega_0 \leq (E_1(\mathbf{k}=0) - E_2(\mathbf{k}=0)) \equiv D = 8 J_{AB}$$
 (13)

and

$$\omega_1 \leq D. \tag{14}$$

In order to get an idea of the relative values of Γ in these systems, we make the following *crude* assumption: we take $\omega_0 = \omega_1 = D$ for each of the three systems (D of course depends on the system). We then find the scattering rate due to one phonon processes to be (ω_D is the Debye frequency in cm⁻¹)

$$\Gamma_1^{(1)} = \eta_1 (D/\omega_D)^3 \,\bar{n}(D), \tag{15}$$

$$\Gamma_2^{(1)} = \eta_2 (D/\omega_D)^3 [\bar{n}(D) + 1], \tag{16}$$

where η_i contains the square of the electron-phonon coupling constants as well as other constants, and has units of energy. Since the width of the spectral lines is directly proportional to this scattering rate, we predict by comparing Eqs. (15) and (16) to Eq. (2) the parameter E in the fit is equal to D_i ; thus,

$$G_2 = \eta_2 (D/\omega_D)^3,$$
 (17)

$$G_1 = \eta_1 (D/\omega_D)^3.$$
(18)

The prediction that $E \cong D$ is quantitatively correct within experimental error.

We may now use Eqs. (17) and (18) together with the data of Table I to calculate η_1/ω_D and η_2/ω_D which we present in Table III.

Some things are evident from Table III. First of all, phenazine is an example of a moderately strongly coupled electron phonon system, while anthracene and naphthalene are examples of weakly coupled systems. This agrees with earlier work⁷ in which the strong exciton-phonon coupling in phenazine was used to explain the temperature dependence of the dimer splitting. There is no observable tempera-

TABLE III. Values of exciton-phonon coupling strength (in units of Debye frequency) for anthracene, naphthalene, and phenazine.

	Anthracene	Naphthalene	Phenazine
η_1/ω_D	0.25	0.67	2.4
η_2/ω_D	0.40	0.67	1.0

ture dependence of that splitting in anthracene and naphthalene.

The reason why phenazine is a more strongly coupled electron-phonon system than naphthalene and anthracene can be understood from the crystal structure. Assume that the major part of the electron-phonon interaction is due to phonon modulation of the van der Waals interactions which give rise to the site energy shifts and not to phonon modulation of the transfer matrix elements J. Then the magnitude of the electron-phonon coupling is proportional to the derivative of the van der Waals interaction between molecules. Since the van der Waals interaction is proportional to R^{-6} (R being an intermolecular distance), we find that the electron-phonon coupling constant varies as R^{-7} . The nearestneighbor distance in phenazine is $\sim 20\%$ smaller than that in anthracene, which would give rise to an electron-phonon coupling constant in phenazine approximately 3.5 times that in anthracene, or a value of η equal to ten times that in anthracene. This is in remarkably good agreement with the data in Table III.

Is it possible to go beyond these crude approximations and learn more details of the electron-phonon coupling in these systems? We believe the answer is no. If experimental data on the k dependence of the scattering rate were available [from electron-paramagnetic reference (EPR) or spinecho experiments, e.g.], our judgment might be different. However, at the present time we believe that further refinement of the data is unnecessary, especially since the calculation of electron-phonon coupling constants is, at present, unfeasible.

B. Zero temperature line shape

The zero temperature spectral line is dominated, in good crystals, by isotopic scattering. In our case, the major scatterers will be molecules containing ¹³C or ¹⁵N substituted in various positions. Happily, the shifts in excitation energy due to ¹³C substitution in various positions in anthracene, naphthalene, and phenazine⁸ are known, so that standard methods such as the coherent potential approximation (CPA) can be applied to this problem^{3,9,10} using the known natural abundances of the isotopes. Since this method is well known, we will not repeat the derivations here. However, in the Appendix we derive the analytic expression for the density of states in the exciton band structure exhibited by these crystals.

In Table IV, we give the excitation energy shifts for isotopic substitutions in anthracene, naphthalene, and phenazine.

Notice that the ratios of ¹³C isotopic shift to bandwidth in naphthalene are large compared to those of anthracene

TABLE IV. Energy shifts of isotopically (singly) substituted molecules. In anthracene there are four α , four β , four δ , and two γ sites; in naphthalene, four α , four β , and two δ sites; in phenazine there are four α , four β , and two δ sites; on the γ site.

Site/isotope	Anthracene	Naphthalene	Phenazine
α/ ¹³ C	+1.2 cm ⁻¹	$+ 3.5 \text{ cm}^{-1}$	$+ 1.35 \text{ cm}^{-1}$
β/ ¹³ C	$+0.7 \text{ cm}^{-1}$	$+ 1.7 \text{ cm}^{-1}$	+0.95 cm ⁻¹
δ/ ¹³ C	$+ 1.05 \text{ cm}^{-1}$	+2.1 cm ⁻¹	$+ 1.35 \text{ cm}^{-1}$
γ/ ¹³ C	+3.0 cm ⁻¹	• • •	•••
¹⁵ N	•••		2.75 cm ⁻¹

and phenazine. This implies that these impurities are neither well *amalgamated* into the exciton band nor *well* split off from the nonsubstituted molecules.¹¹ Therefore, we would expect that the CPA will not be as accurate for line shapes in this case as in the other cases. In addition, the α -substituted ¹³C naphthalene is at an energy *resonant* with the upper k = 0 exciton state (at the top of the band). This will cause severe scattering and intensity borrowing for that optical line. The experimental spectrum is indeed very complex at that energy.¹¹ We expect, therefore, that the CPA, although



FIG. 6. The calculated line shape at T = 0 due to isotopic scattering in anthracene: (a) lower component; (b) upper component with phonon emission rate Γ of 0.5 cm⁻¹. All energies are in cm⁻¹.

-6.65

-5.60

6.



5.



reasonable for line *positions*, will be unable to handle the line *shapes* very well.

3.

ENERGY

2.

INTENSITY

(a)

INTENSITY

(b)

-5.85

-5.90

-5.80

-5.75

ENERGY

-5.70

We have solved the CPA equations numerically for these three systems and calculate the optical spectral intensities at T = 0 within the CPA. The results are presented in Figs. 6, 7, and 8.

In Fig. 6, we see the predicted line shapes for anthracene. For the lower Davydov component, we predict an anisotropic line of width 0.008 cm^{-1} in good agreement with experiment. For the upper component, we predict a symmetric line of width 0.2 cm⁻¹ in the absence of phonon emission broadening. This is in reasonable agreement with the experimental (see Table I) result for $\Gamma_2^{(0)}$, when phonon scattering is taken into account (the plot of Fig. 6 includes the T = 0 phonon emission contribution).

In Fig. 7, we see the predicted line shapes for naphthalene. The lower Davydov component is predicted to have an anisotropic linewidth of 0.02 cm^{-1} and the experimental re-



FIG. 8. The calculated line shape at T = 0 due to isotopic scattering in phenazine: (a) lower component; (b) upper component with a phonon emission rate Γ of 0.025 cm⁻¹. All energies are in cm⁻¹.

sult is 0.07 cm^{-1} . The upper component is predicted to be broad and very distorted. As we pointed out already, the CPA does not do well in this case because of the effects mentioned above.

In Fig. 8, we present the line shapes for phenazine. The lower component is predicted to have a width of 0.010 cm^{-1} (experiment 0.0065 cm^{-1}). The upper component is predicted to have a width of 0.10 cm^{-1} in the absence of phonon emission (experimental $\Gamma_2^{(0)} = 0.11 \text{ cm}^{-1}$). We have included the phonon emission broadening of 0.025 cm^{-1} in presenting Fig. 8(b). Although the line shape of the upper component is predicted to be rather asymmetric in the *absence* of phonon emission, Fig. 8(b) shows that even a small amount of phonon broadening tends to make the line symmetric, as is observed in the experiment.

IV. CONCLUSIONS

The results of this paper indicate that a reasonably good quantitative fit of the linewidths (and positions) of the exciton lines in anthracene, naphthalene, and phenazine single crystals can be found with a simple theoretical model including isotopic impurity scattering phonon-exciton coupling. The effects of the exciton and band *structure* (rather than just the width) are quite clear when one compares these three systems with similar bandwidths, but different structures.

There are still unanswered theoretical questions about these systems. The most interesting, and potentially important, is how to treat the isotopic scattering, including the resonance effects, in naphthalene. The CPA clearly fails in this case for the upper component, and in addition, is not particularly good for the lower component. Since the isotopic scattering in this case is neither in the amalgamation or split-band limits, the CPA does not work as well as in the cases of anthracene and phenazine. Finally, the lower component in phenazine is predicted to be broader than it is experimentally; the reason for this discrepancy is unclear. It may be due to small errors in the isotopic energy defects (Table IV). We have examined the effect of lowering the α and δ energy defects by 25%. This changes the predicted linewidth to be closer to the experiment (0.009 vs 0.0065 cm^{-1}), but no quantitative agreement is reached. We have also used the effective J_{AA} and J_{AB} values given in Table II instead of the measured values. Using these, the linewidth in phenazine is predicted to be 0.009 cm^{-1} , so that the effect of the nonnearest neighbors is small, at least when treated in this way.

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APPENDIX

The exciton band structure for all three systems can be written in the extended zone scheme

$$\epsilon(k) = 2J_{AA} \cos k_1 + 4J_{AB} \cos \frac{k_1}{2} \cos \frac{k_2}{2},$$
 (A1)

where

$$-2\pi < k_1 \le +2\pi,$$

$$-2\pi < k_2 \le +2\pi.$$
 (A2)

The zeroth order Green function can be written

$$G^{(0)}(z) = \frac{1}{N} \sum_{k_1, k_2} [z - \epsilon(k)]^{-1}$$
(A3)
= $(4\pi)^{-2} \int dk_1 dk_2 \Big[z - 2J_{AA} \cos k_1$
 $- 4J_{AB} \cos \frac{k_1}{2} \cos \frac{k_2}{2} \Big]^{-1}.$ (A4)

The density of states is related to $G^{(0)}(z)$ by

$$\rho(z) = \pi^{-1} \operatorname{Im} G(0) (z - i\epsilon) \tag{A5}$$

in the limit $\epsilon \rightarrow 0$.

Notice that for $|J_{AB}/J_{AA}| = \delta > 2$ the extrema of the ex-

citon band occur at $\epsilon = 2J_{AA}(1 \pm 2\delta)$ (the two Davydov components). However, for $\delta < 2$, the extrema occur at

$$\epsilon_1 = 2J_{AA}(1+2\delta) \tag{A6}$$

and

$$\epsilon_2 = -2J_{AA}(1+\delta^2/2).$$
 (A7)

The integral over k_2 in Eqs. (A4) can be done immediately to give

$$G^{(0)}(z) = \frac{1}{4\pi} \int_{-2\pi}^{2\pi} dk_1 \left[(z - 2J_{AA} \cos k_1)^2 - \left(4J_{AB} \cos \frac{k_1}{2} \right)^2 \right]^{1/2}.$$
 (A8)

Defining $t = \cos k$, we find

$$G^{(0)}(z) = \frac{1}{2\pi |J_{AA}|} \int_{-1}^{+1} dt \{ (1-t^2) [t^2 - (2u+2\delta^2)t + (u^2 - 2\delta^2)] \}^{-1/2},$$
 (A9)

where $u = z/2J_{AA}$, or

$$G^{(0)}(z) = \frac{1}{2\pi |J_{AA}|} \times \int_{-1}^{+1} dt \{ (1-t^2)(t-\lambda_+)(t-\lambda_-) \}^{-1/2}$$
(A10)

with

$$\lambda_{+} = (u + \delta^{2}) \pm \delta (2 + \delta^{2} + 2u)^{1/2}.$$
 (A11)

In the band, λ_{\pm} are real. For $\delta > 2$, $\lambda_{+} > 1$. For $\delta < 2$, $\lambda_{+} > 1$ for $1 - 2\delta < u \le 1 + 2\delta$, but $\lambda_{+} < 1$ for $-(1 + \delta^{2}/2) \le u < 1 - 2\delta$. Thus for $1 - 2\delta < u \le 1 + 2\delta$,

$$\rho(z) = \frac{1}{2\pi^2 |J_{AA}|} \int_{\lambda_-}^{1} dt \{ (1-t^2)(\lambda_+ -t)(t-\lambda_-) \}^{-1/2}$$
$$= \frac{1}{2\pi^2 |J_{AA}|} [2(\lambda_+ -\lambda_-)]^{-1/2} K(\mu), \qquad (A12)$$

where K(u) is the complete elliptic integral of the first kind and

$$\mu = \left\{ \frac{(1 - \lambda_{-})(1_{+}\lambda_{+})}{2(\lambda_{+} - \lambda_{-})} \right\}^{1/2}.$$
 (A13)

For
$$-(1 + \delta^2/2) < u < (1 - 2\delta)$$
,

$$\rho(z) = \frac{1}{2\pi^2 J_{AA}} \int_{\lambda_-}^{\lambda_+} dt \{ (1 - t^2) (\lambda_+ - t) (t - \lambda_-) \}^{-1/2}$$
(A14)

$$=\frac{1}{\pi^2 J_{AA}} [(1-\lambda_-)(1+\lambda_+)]^{-1/2} K\left(\frac{1}{\mu}\right).$$
(A15)

Using this form of $\rho(z)$, we can compute all the functions needed in the CPA equations.

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