# COMMENTS ON EXCITON-PHONON COUPLING. II. VARIATIONAL SOLUTIONS\*

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Two variational calculations of the energy and correlation functions for a simple exciton-phonon coupled system are presented and contrasted to the adiabatic solution and the exact solution. The simpler variational solution leads to two minima and abrupt changes in the properties of the system; an asymmetric variational wavefunction, motivated by the form of perturbation theory for this problem, leads to smooth behavior in agreement with the exact result.

# 1. Introduction

A recent variational calculation of the free energy of an exciton interacting with Einstein [1] phonons produced a free energy surface with two minima as a function of the variational parameter. This result held for a one-dimensional system as well as higher dimensionality. It is possible, however, to show that in the adiabatic approximation, there will be only one minimum in the energy surface in one dimension [2]. Although the calculation of ref. [1] is not adiabatic, this argument [2] has led us to re-examine the variational calculation in an attempt to understand at a more fundamental level the origin of the two minima.

The importance of this matter is quickly enough discerned. There have been several theoretical calculations concerned with abrupt conductivity transitions in insulators due to the large changes in the small polaron mobility resulting from changes in the state of the small polaron [2]. The small polaron states were found from a variational wavefunction. The possibility of producing spurious minima in the energy surface (each minimum corresponds to a state

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\*\* Present address: Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, USA. of the small polaron) may seriously complicate such theories. This happens because the resultant temperature dependent appearance or disappearance of these states could lead to the prediction of spurious transitions.

Although it would be ideal to be able to assess beforehand the number of minima the energy surface should have for a given hamiltonian, this is not feasible. Thus, for a variational calculation, one cannot be certain that sufficient flexibility has been allowed for in order that the different kinds of states are adequately differentiated or even to guard against the introduction of spurious states. The matter is further complicated by the use of the Born-Oppenheimer and adiabatic approximations. This occurs because we want to be able to dinstinguish between shortcomings that are the result of a mathematical technique and those that are the result of approximations to the physics.

In lieu of a general theory of these shortcomings, our approach is to examine a model in all of the various methods and approximations, but one which is amenable to unambiguous solution (i.e. the exact result is known). The exciton *dimer* in the limit of linear exciton—phonon coupling has been selected for this purpose. This model is discussed in detail in section 2 where the known facts about the model are collected and where some variational results are presented. In effect, the problem we are addressing in this paper is posed in the context of the dimer model.

The results are discussed in section 3. Briefly stated, it is found that while the adiabatic energy does not exhibit two minima and the exact energy does not show any discontinuous behavior (which might arise from two minima), the simple variational result has two minima and discontinuous behavior. In addition, a slightly more flexible variational form has no discontinuous behavior indicating that it is the simple form of the variational wavefunction that is at fault.

## 2. The exciton dimer

### 2.1. The hamiltonian and exact eigenfunction

The hamiltonian for the exciton dimer with linear exciton phonon coupling is given by

$$H = J\omega(A_1^*A_2 + A_2^*A_1)$$
  
+  $\sum_{n=1}^{2} \{EA_n^*A_n + \frac{1}{2}P_n^2 + \frac{1}{2}\omega^2 Q_n^2$   
-  $2^{1/2}g\omega^{3/2}Q_n A_n^*A_n\},$  (2.1)

where  $A_n^*(A_n)$  creates (destroys) an excitation with energy E on site n,  $P_n$  and  $Q_n$  are the local vibrational momentum and coordinate at site n (weighted so that the mass does not appear), J is the matrix element of H between states with the excitation on different sites (i.e. the hopping or transfer integral) and g is a dimensionless coupling constant giving the strength of the excitation phonon coupling. If phonon creation and annihilation operators,  $B_n^*$  and  $B_n$ , are defined in the usual way, then

$$H = J\omega(A_1^*A_2 + A_2^*A_1) + \sum_{n=1}^{2} \{EA_n^*A_n + \omega(B_n^*B_n + \frac{1}{2}) -g\omega A_n^*A_n(B_n + B_n^*)\}.$$
 (2.2)

Since we will only be concerned with one exciton states, we can choose to reckon energy from the value  $E + \omega$  (the zero point energy plus the exciton energy). Dividing H by  $\omega$ , so that all energies are measured in units of the phonon frequency  $\omega$ , we find

$$h_{1} = H/\omega = J(A_{1}^{*}A_{2} + A_{2}^{*}A_{1}) + \sum_{n=1}^{2} \{B_{n}^{*}B_{n} - gA_{n}^{*}A_{n}(B_{n} + B_{n}^{*})\}.$$
(2.3)

Note that this differs slightly from the treatment of Suna [3], who divides H by the "polaron" binding energy  $E_{\rm B} = \frac{1}{2}g^2\omega$ . In the k-representation, which in this case reduces to defining new operators R from the original  $R_n$  by

$$R_{\pm} = \frac{1}{2}(R_1 \pm R_2),$$

we find

$$h_{1} = J(A_{+}^{*}A_{+} - A_{-}^{*}A_{-}) + (B_{+}^{*}B_{+} + B_{-}^{*}B_{-})$$
  
-(g/2<sup>1/2</sup>) {( $B_{+}^{`} + B_{+}^{*}$ ) ( $A_{+}^{*}A_{+} + A_{-}^{*}A_{-}$ )  
+ ( $B_{-} + B_{-}^{*}$ ) ( $A_{+}^{*}A_{-} + A_{-}^{*}A_{+}$ )}. (2.4)

This representation shows clearly that in one-exciton space, where  $A_{+}^{*}A_{+} + A_{-}^{*}A_{-} = 1$ , the exciton-phonon coupling to the + vibrations can be removed by a simple change in definition of  $B_{+}$  and  $B_{+}^{*}$ :

$$B'_{+} = B_{+} - g/2^{1/2}, \qquad B'^{*}_{+} = B^{*}_{+} - g/2^{1/2}.$$
 (2.5)

Then,

$$h_{2} = J(A_{+}^{*}A_{+} - A_{-}^{*}A_{-}) + B_{+}^{'*}B_{+}^{'} + B_{-}^{*}B_{-} - g^{2}/2$$
$$- (g/2^{1/2})(A_{+}^{*}A_{-} + A_{-}^{*}A_{+})(B_{-} + B_{-}^{*}).$$
(2.6)

Since  $B'_{+}B'_{+}$  is a constant of motion, and  $g^2/2$  is just an additive constant, we can neglect them in the following. The hamiltonian we have to deal with is then

$$h = J(A_{+}^{*}A_{+} - A_{-}^{*}A_{-}) + B_{-}^{*}B_{-}$$
$$- (g/2^{1/2})(A_{+}^{*}A_{-} + A_{-}^{*}A_{+})(B_{-} + B_{-}^{*}), \qquad (2.7)$$

which describes two closely spaced electronic states coupled by a single vibration. This is isomorphic to a pseudo-Jahn-Teller effect hamiltonian [4]. If  $\epsilon_{\alpha}$  is an eigenvalue of h [eq. (2.7)] then the eigenvalue of H is given by

$$E_{\alpha} = \omega(\epsilon_{\alpha} - g^2/2) + E + \omega + n_{+}\omega, \qquad (2.8)$$

where  $n_+$  is the eigenvalue of  $B'_+B'_+$ .

Many authors have solved eq. (2.7) numerically to find the low lying eigenvalues and eigenfunctions. In the present section we will be concerned with the lowest state in one exciton space only, and in particular, with various approximations to the energy and the wavefunction which will be compared to the exact result. The exact lowest eigenfunction (in oneexciton space) can be written

$$\phi = \sum_{n=0}^{\infty} \left\{ C_{2n} A_{+}^{*} (B_{-}^{*})^{2n} / \left[ (2n)! \right]^{1/2} + C_{2n+1} A_{-}^{*} (B_{-}^{*})^{2n+1} / \left[ (2n+1)! \right]^{1/2} \right\} |0\rangle, \quad (2.9)$$

where we have assumed J < 0 for convenience. In the limit g = 0,  $C_n = \delta_{n0}$ ; in the limit J = 0,

$$C_n = \{(-g/2^{1/2})^n/(n!)^{1/2}\} \exp(-\frac{1}{4}g^2).$$

We have found  $\phi$  numerically by diagonalizing the matrix representing h using up to 30 functions. Thus, in our case, the sum in (2.9) is cut off at  $n \approx 15$ . The coefficients can be assumed real.

In order to assess the character of this state, we will use two measures of exciton—phonon correlation. The first is the number of quanta of vibration relative to that number when J = 0, and is given by

$$\langle N_{\rm P} \rangle \equiv (2/g^2) \langle \phi | B_{-}^* B_{-} | \phi \rangle = \sum_{n=0}^{\infty} C_n^2 n(2/g^2).$$
 (2.10)

The second was introduced by Suna and given by  $\boldsymbol{\delta},$  where

$$\delta = (2^{1/2}g)^{-1} |\langle \phi | (A_+^*A_- + A_-^*A_+) (B_- + B_-^*) | \phi \rangle|$$
  
=  $(2^{1/2}/g) \left| \sum_{n=0}^{\infty} C_n C_{n+1} (n+1)^{1/2} \right|.$  (2.11)

The factor  $2^{1/2}g$  is the value of the matrix element in the limit J = 0, thus  $\delta = 1$  when the exciton and the phonon are completely correlated (J = 0).

#### 2.2. Simple variational calculation

In treating exciton-phonon coupling and electronphonon coupling (e.g. polarons) in insulating crystals, a simple variational procedure is frequently employed [1,5]. In the case of a dimer this procedure would reduce to

$$\widetilde{\phi} = \exp\left\{-(\widetilde{g}/2^{1/2})(A_{+}^{*}A_{-} + A_{-}^{*}A_{+})(B_{-}-B_{-}^{*})\right\}A_{+}^{*}|0\rangle,$$
(2.12)

where the parameter  $\tilde{g}$  is varied to find a minimum in the expectation value of h in state  $\tilde{\phi}$ . The motivation for the form of  $\tilde{\phi}$  is that in the limit J = 0 setting  $\tilde{g} = g$  gives the exact state. In addition, for g = 0 $(J \neq 0)$ , setting  $\tilde{g} = g = 0$  gives the exact eigenstate again. Thus the state  $\tilde{\phi}$  has the correct form in the limits g/J = 0 and  $g/J \rightarrow \infty$ . With this form, we find

$$\widetilde{\epsilon} = J \exp(-\widetilde{g}^2) + \frac{1}{2}\widetilde{g}^2 - g\widetilde{g}, \qquad (2.13)$$

so that setting  $\partial \tilde{\epsilon} / \partial \tilde{g} = 0$  gives

$$\widetilde{g} = g[1+2|J|\exp(-g^2)]^{-1}.$$
 (2.14)

This equation may have multiple solutions depending on the values of J and g. In appendix A, we derive the conditions for two minima in the  $\tilde{\epsilon}$  versus g curve. In the polaron and exciton cases, this has been taken to imply the existence of two states with similar energies and very different properties. For example, one of these states has small exciton phonon correlation ( $\delta$  or  $\langle N_p \rangle$ ) while the other has large correlation. In addition, variational calculations of the free energy [1,2] have shown that, within this approximation, which of these two states is lower in free energy changes with temperature, so a rather abrupt change in the properties of the lowest state is predicted. This can also be inferred from the change in  $\tilde{\epsilon}$  with increasing g (which is often taken to be proportional to temperature); as g increases from zero at constant J, the nature of the lower state changes abruptly from delocalized (small e-p correlation) to localized (large e-p correlation). This appearance of these two types of states coexisting for a single value of g for the dimer and for the one-dimensional exciton is unexpected since rather general arguments [2] seem to preclude this behavior in these low dimensional systems, while not ruling it out for three dimensions.

In order to compare these results with the exact results, we derive formulas for the exciton-phonon correlation functions,  $\delta$  and  $\langle \tilde{N}_p \rangle$ :

$$\langle \widetilde{\mathcal{W}} \rangle = \langle \widetilde{\phi} | B_{-}^{*} B_{-} | \widetilde{\phi} \rangle (2/g^{2}) = \langle \widetilde{g} / g \rangle^{2}, \qquad (2.15)$$

$$\widetilde{\delta} = |\langle \widetilde{\phi} | (A_{+}^{*}A_{-} + A_{-}^{*}A_{+}) (B_{-} + B_{+}^{*}) | \widetilde{\phi} \rangle |(2^{1/2}g)^{-1} = (\widetilde{g}/g).$$
(2.16)

These formulas are derived using the standard procedures in appendix B. We will compare these to the exact results below. We note parenthetically that the overlap of  $\tilde{\phi}$  with the exact wavefunction never falls below  $\approx 0.9$ , so that it seems that  $\tilde{\phi}$  is quite close to  $\phi_{\text{exact}}$ .

### 2.3. Asymmetric variational calculation

In order to examine the variational results more closely, we will introduce an asymmetric variational function below. To motivate the discussion, consider the eigenstate near g = 0. The lowest order approximation is

$$\phi^{(0)} = A_{\pm}^{*}[0). \tag{2.17}$$

Using this as a zeroth order function in a perturbation calculation with the perturbation, V, given by the term proportional to g in h [eq. (2.7)], we find (J < 0)

$$\phi = A_{+}^{*}|0\rangle + \frac{g}{2^{1/2}(2|J|+1)} A^{*}B_{-}^{*}|0\rangle + \frac{g^{2}}{4(2|J|+1)} A_{+}^{*}(B_{+}^{*})^{2}|0\rangle + \dots, \qquad (2.18)$$

whereas  $\widetilde{\phi}$  [eq. (2.12)] when expanded gives

$$\widetilde{\phi} = \{A_{+}^{*}|0\rangle + (\widetilde{g}/2^{1/2})A_{-}^{*}B_{-}^{*}|0\rangle + \frac{1}{4}\widetilde{g}^{2}A_{+}^{*}(B_{+}^{*})^{2}|0\rangle + ...\}\exp(-\frac{1}{4}\widetilde{g}^{2}).$$
(2.19)

Comparing (2.18) and (2.19) we see that  $\phi$  fails to give the correct ratio of the first three coefficients no matter how g is chosen. In order for these coefficients to be given correctly, a more flexible variational function must be used. The simplest one is

$$\widetilde{\psi} \approx \exp\left\{ (\widetilde{g}_1 A_+^* A_- + \widetilde{g}_2 A_-^* A_+) (B_- - B_-^*) \right\} A_+^* | 0 \rangle.$$
(2.20)

This function is unnormalized since the transformation in (2.20) is not unitary; however, it can easily be normalized by dividing by  $\langle \tilde{\psi} | \tilde{\psi} \rangle^{1/2}$ . This form will be flexible enough to reproduce eq. (2.18) at small g, and in addition will reproduce the correct form of  $\phi$ at large g, which the variational function  $\phi$  can do also since, in this limit,  $\tilde{g} = g$  in eq. (2.12) or  $\tilde{g}_1 = \tilde{g}_2 =$ g in eq. (2.20).

The introduction of two variational parameters makes the calculation much more difficult and time consuming; we investigated instead the one-parameter form  $\widetilde{g}_1 = -(g/2^{1/2}), \widetilde{g}_2 = -(g/2^{1/2}) \alpha$  so that

$$\widetilde{\phi} = \exp\left\{-(g/2^{1/2})(A_{+}^{*}A_{-}^{+}\alpha A_{-}^{*}A_{+})(B_{-}^{-}B_{-}^{*})\right\}A_{+}^{*}|0\rangle.$$
(2.21)

This (unnormalized) function has the flexibility to be correct to  $O(g^2)$  at small g [where  $\alpha \approx (2|J|+1)^{-1}$ ] and to be correct at very large g (where  $\alpha \approx 1$ ).

Using this form, we compute in appendix C the energy and two-correlation functions. The results are

$$\widetilde{\widetilde{\epsilon}} = -|J| \left[ \frac{(1-\alpha)+(1+\alpha)e^{-g^2\alpha}}{(1+\alpha)+(1-\alpha)e^{-g^2\alpha}} \right] + \frac{g^2\alpha(\alpha-1)}{(1+\alpha)+(1-\alpha)e^{-g^2\alpha}} - \frac{g^2\alpha}{2}, \qquad (2.22)$$

$$\approx \widetilde{N} = \alpha [(1 + \alpha) - (1 - \alpha)e^{-g^2\alpha}] \times [(1 + \alpha) + (1 - \alpha)e^{-g^2\alpha}]^{-1}$$
(2.23)

$$\widetilde{\delta} = 2\alpha/[(1+\alpha) + (1-\alpha)e^{-g^2\alpha}].$$
(2.24)

Even with one variational parameter, the energy,  $\tilde{\epsilon}$ , is complicated enough that finding the minimum is a complex matter. We resorted to a hand calculator to compute  $\tilde{\epsilon}$  versus  $\alpha$  for each value of J and g and found the minimum by inspection. There is only one minimum for all values of J and g investigated. We will discuss the values of  $\tilde{\epsilon}_{\min}$ ,  $\langle \tilde{N}_{\rm P} \rangle_{\min}$  and  $\tilde{\delta}_{\min}$  below.

# 2.4. Adiabatic calculation

The eigenvalues of h can be found approximately by using the adiabatic approximation [3]. To do this, we must neglect the vibrational kinetic energy; transforming the phonon variables  $(B_{-} \text{ and } B_{-}^{*})$  back to momentum and coordinate  $(P_{-} \text{ and } Q_{-})$  we find:

$$h = J(A_{+}^{*}A_{+} - A_{-}^{*}A_{-}) + \frac{1}{2}\omega^{-1}P_{-}^{2} + \frac{1}{2}\omega Q_{-}^{2} - \frac{1}{2}$$
$$-g\omega^{1/2}Q_{-}(A_{+}^{*}A_{-} + A_{-}^{*}A_{+}). \qquad (2.25)$$

Neglecting the term  $(1/2)P_{-}^2$  we can solve for the electronic wavefunction and energy (which are both functions of  $Q_{-}$ ), in the usual way. The lowest energy state is written

$$\phi_{\rm A} = C_+ A_+^* |0\rangle + C_- A_-^* |0\rangle, \qquad (2.26)$$

and the eigenvalue (i.e. the adiabatic potential) is

$$\epsilon_{\rm A} = -(J^2 + g^2 \omega Q_{-}^2)^{1/2} + \frac{1}{2} \omega Q_{-}^2, \qquad (2.27)$$

where we have added 1/2, the zero point energy in these units, in order to compare with the earlier results. The minimum of  $\epsilon_A$  is at  $Q_- = 0$  for  $J^2 > g^4$ and at  $Q_- = \pm [(g^4 - J^2)/g^2\omega]^{1/2}$  for  $J^2 < g^4$ . The different signs in the latter case refer to two possible (and degenerate) electronic states which are semilocalized. By this is meant that the probability density on site 1 is different from the probability density on site 2 for these configurations. This is summarized below

$$\begin{aligned} \epsilon_{A,\min} &= -|J|, \\ (C_{+})_{\min} &= 1, \quad (C_{-})_{\min} &= 0, \\ (Q_{-})_{\min} &= 0; \end{aligned} \right\} J^{2} > g^{4}; \quad (2.28)$$

$$\begin{aligned} & \epsilon_{\text{A,min}} = -\frac{1}{2}g^2 - \frac{1}{2}J^2/g^2, \\ & (C_{\pm})_{\text{min}} = \left[\frac{1}{2}(1 \pm |J|/g^2)\right]^{1/2}, \\ & (Q_{-})_{\text{min}}^2 = (g^4 - J^2)g^2\omega. \end{aligned} \right\} J^2 < g^4. \end{aligned} \tag{2.29}$$

The amplitudes of excitation at sites 1 and 2 are given by

$$C_1 = 2^{-1/2}(C_+ + C_-), \quad C_2 = 2^{-1/2}(C_+ - C_-), \quad (2.30)$$

thus

$$J^2 > g^4 |C_1|^2 = |C_2|^2 = 1/2$$

Table 1 Comparison of energies and correlation functions

$$J^{2} < g^{4} |C_{1}|^{2} = \frac{1}{2} + \frac{1}{2}(1 - J^{2}/g^{4})^{1/2}, \qquad (2.31)$$

$$|C_2|^2 = \frac{1}{2} - \frac{1}{2}(1 - J^2/g^4)^{1/2}.$$
 (2.32)

The latter values are for one of the two degenerate minima (i.e. that at  $(Q_{-})_{min} = +(g^4 - J^2/g^2 \omega)^{1/2})$ . Note that these two degenerate minima are dictated by the symmetry of the system.

The effect of the nuclear kinetic energy operator will be to "mix" these two possible configurations (i.e. two values of  $(Q_{-})_{min}$ ), since the adiabatic potential is a double well. We will neglect this in what follows and use the lowest order adiabatic states as approximations to the eigenstate. The exciton-phonon correlation functions  $\delta$  can be calculated for these states also and we find

$$\delta_{A} = 2C_{+}C_{-}(Q_{-})_{J}/(Q_{-})_{J=0},$$

SO

$$\delta_{\rm A} = (1 - x^2), \quad x^2 \equiv J^2/g^4 < 1,$$
  
 $\delta_{\rm A} = 0, \qquad x^2 > 1.$ 

# 2.5. Comparison of approximate theories

Using the results of sections 2.2-2.4, we can compute the values of the energy and correlation functions

g²	E				$\langle N \rangle$			δ			
	exact	Ē	~ e	۴A	exact	<ñ>>	$\langle \widetilde{\widetilde{N}} \rangle$	exact	δ	š	δ <sub>A</sub>
J = -	-2										
1 2 3 4 5 6	-2.109 -2.244 -2.419 -2.662 -2.987 -3.381	-2.101 -2.206 -2.317 -2.433 -2.563 -3.005	-2.109 -2.239 -2.400 -2.605 -2.878 -3.245	-2.000 -2.000 -2.167 -2.500 -2.900 -3.333	0.074 0.136 0.252 0.446 0.659 0.803	0.041 0.046 0.051 0.057 0.927 0.978	0.071 0.108 0.212 0.380 0.576 0.719	0.240 0.303 0.409 0.567 0.729 0.836	0.202 0.214 0.225 0.238 0.963 0.989	0.238 0.281 0.312 0.394 0.563 0.745	0 0 0.555 0.750 0.840 0.889
J = .	-1										
1 2 3 4 5 6	-1.188 -1.437 -1.766 -2.171 -2.622 -3.095	-1.174 -1.365 -1.600 -2.024 -2.508 -3.002	-1.187 -1.427 -1.736 -2.125 -2.575 -3.052	-1.000 -1.250 -1.666 -2.125 -2.600 -3.083	0.214 0.394 0.629 0.813 0.907 0.950	0.130 0.171 0.325 0.898 0.970 0.988	0.211 0.318 0.481 0.641 0.755 0.809	0.430 0.571 0.745 0.866 0.929 0.960	0.360 0.413 0.570 0.948 0.985 0.994	0.424 0.526 0.663 0.783 0.861 0.894	0 0.750 0.889 0.938 0.960 0.972



Fig. 1. Exciton-phonon correlation,  $\delta$ , as a function of  $g^2$  for J = -1. Solid line: adiabatic theory; dashed line: simple variational theory; dotted line: asymmetric variational theory; dot-dash line: exact result.

for the exact and approximate theories. In table 1, we present, for two values of J and a number of values of g, this comparison. In figs. 1 and 2, we compare the calculated values of  $\delta$  as a function of g and in figs. 3 and 4, we compare the calculated values of





Fig. 3. The number of phonons N associated with lowest state as a function of  $g^2$  for J = -1. Dashed line: simple variational theory; dotted line: asymmetric variational theory; solid line: exact theory.

 $\langle N \rangle$  for two values of J.

Note that the simple variational function has an abrupt change in its properties as g increases for |J| = 2. This is due to there being two minima in the variational energy as a function of g. Although the exact



function changes very quickly in this region of g, it does so in a smooth fashion. This will be discussed in detail in the next section. The asymmetric variational function does not show two minima or an abrupt change.

The general characteristics of the three approximate solutions can be seen from the figures and table. In particular, the simple variational function is undercorrelated for  $g^2 \leq |J|$  and overcorrelated for  $g^2 \geq |J|$ ; on the other hand, the asymmetric variational function is correct at small g but undercorrelated for large g. In addition, the adiabatic function is undercorrelated at small g and overcorrelated at large g. Moreover, the simple variational form gives a rather poor energy as  $g^2$  gets large while the asymmetric variational form and the adiabatic wavefunction give rather good energies in this region.

# 3. Discussion

The results presented above indicate that:

(i) in the adiabatic approximation, there is only one minimum in the energy surface, in agreement with the arguments in ref. [2];

(ii) in the exact solution, there is no discontinuity in either of the exciton-phonon correlation functions, although there is a rapid change in both as the exciton-phonon coupling is increased;

(iii) in the simple variational solution, there are two minima in the energy surface (as a function of variational parameter) which leads to a discontinuity in the correlation functions; (iv) the failure of the simple variational result can be remedied by allowing the variational form to be slightly more flexible; this leads to nondiscontinuous correlation functions and a single minimum in the energy surface.

The abrupt change in the simple variational result is reminiscent of the results of unrestricted Hartree— Fock theory (UHF) [6] where the character of the variational lowest energy wavefunction (constrained to be a single determinant) changes dramatically as the parameters of the system are varied. In that case, the variational wavefunction may become a spin density wave or a charge density wave with certain correlation functions exhibiting sharp changes, even though the exact ground state does not exhibit these. In spite of this, the variational function may be useful in discussing curve crossing and other effects.

In the present case, even though the simple variational solution shows incorrect behavior as far as the number of minima in the energy surface and the presence of a discontinuous change in certain properties, it is still approximately correct in the value of the energy as well as being qualitatively accurate for the correlation functions for g small and g large. In addition, for J small enough so that two minima do not occur, it is reasonably accurate. However, it is clear that for J large enough so that two minima are predicted, the simple variational result will give inaccurate results for the correlation functions and the abruptness of the transition. In these cases, neither the simple variational result nor the simple adiabatic result is very good for all g.

#### Appendix A

In this appendix, we derive the conditions for the existence of two minima in the simple variational energy,  $\tilde{\epsilon}$ , given by eq. (2.14). The condition for an extremum in the  $\tilde{\epsilon}$  versus  $\tilde{g}$  curve is

$$\widetilde{g}\left[1+2|J|\exp\left(-\widetilde{g}^{2}\right)\right]=g.$$
(A.1)

The lhs of this equation may be graphed as a function of  $\tilde{g}$ . For |J| greater than a certain value, to be found below, this curve has two extrema at values of  $\tilde{g}$  which we label  $\tilde{g}_1$  and  $\tilde{g}_2$ . There will then be three solutions to eq. (A.1), one maximum in  $\tilde{\epsilon}$  versus  $\tilde{g}$  and two minima, for

$$\widetilde{g}_{1}\left[1+2|J|e^{-\widetilde{g}_{1}^{2}}\right] \ge g \ge \widetilde{g}_{2}\left[1+2|J|e^{-\widetilde{g}_{2}^{2}}\right].$$
(A.2)

To find  $\tilde{g}_1$  and  $\tilde{g}_2$ , we note that they are values of  $\tilde{g}$  for which the lhs of eq. (A.1) has an extremum; they are thus given by setting the derivative of the lhs to zero:

$$\frac{1}{2}|J|^{-1} = (2\widetilde{g}_i^2 - 1)\exp(-\widetilde{g}_i^2), \quad i = 1, 2.$$
(A.3)

For this equation to have solutions (and so there be two minima in  $\tilde{\epsilon}$  versus  $\tilde{g}$ ),

$$2|J| > \frac{1}{2}e^{+1.5} = 2.24. \tag{A.4}$$

This is the condition on |J| for there to be two minima; the condition on g is given in (A.2) with  $g_1$  and  $g_2$  given by (A.3). By substituting (A.3) into (A.2) we find the condition on g can be rewritten

$$2\widetilde{g}_1^3/(2\widetilde{g}_1^2-1) \ge g \ge 2\widetilde{g}_2^3/(2\widetilde{g}_2^2-1).$$

For |J| = 2, we find  $\tilde{g}_1 = 0.88$ ,  $\tilde{g}_2 = 1.73$  and two minima exist for  $2.50 \ge g \ge 2.07$ .

# Appendix B

From 
$$\phi$$
 given by eq. (2.12), we will compute  $\langle N \rangle$  and  $\phi$ .

$$\langle N \rangle = \langle \widetilde{\phi} | B_{-}^{*} B_{-} | \widetilde{\phi} \rangle (2/g^{2})$$
  
=  $(2/g^{2})\langle 0 | A_{+} \exp\{(g/2^{1/2})(A_{+}^{*} A_{-} + A_{-}^{*} A_{+})(B_{-} - B_{-}^{*})\}B_{-}^{*} B_{-} \exp\{(g/2^{1/2})(A_{+}^{*} A_{-} + A_{-}^{*} A_{+})(B_{-} - B_{-}^{*})\}A_{+}^{*} | 0 \rangle.$   
(B.1)

By using the formula

$$e^{A}Be^{-A} = B + [A, B] + \frac{1}{2!}[A, [A, B]] + ...,$$
 (B.2)

we find

$$\langle \widetilde{N} \rangle = (2/g^2) \langle 0 | A_+ [B_-^* + \widetilde{g}/2^{1/2} (A_+^* A_- + A_-^* A_+)] [B_- + \widetilde{g}/2^{1/2} (A_+^* A_- + A_-^* A_+)] A_+^* | 0 \rangle,$$
  
$$\langle \widetilde{N} \rangle = (\widetilde{g}/g)^2.$$
 (B.3)

To find  $\delta$ , we note the definition

$$\widetilde{\delta} = (2^{1/2}_{--}g)^{-1} |\langle \widetilde{\phi} | (A_+^*A_- + A_-^*A_+) (B_- + B_-^*) | \widetilde{\phi} \rangle|.$$
(B.4)

Using (B.2) once more,

$$\widetilde{\delta} = (2^{1/2}g)^{-1} \langle 0|A_{+}(A_{+}^{*}A_{-} + A_{-}^{*}A_{+})[B_{-} + B_{-}^{*} + 2^{1/2}\widetilde{g}(A_{+}^{*}A_{-} + A_{-}^{*}A_{+})]A_{+}|0\rangle = (\widetilde{g}/g).$$
(B.5)

# Appendix C

Using the asymmetric variational function,  $\tilde{\phi}$ , given by eq. (2.21), we will compute the energy and correlation functions. First we write  $\phi$  as

$$\widetilde{\phi} = \exp\left\{-g/2^{1/2} \left[A_{+}^{*}A_{-} + \alpha A_{-}^{*}A_{+}\right] \left[B_{-} - B_{-}^{*}\right]\right\} A_{+}^{*} |0\rangle$$

$$= \left\{\cosh g(\alpha/2)^{1/2} \left(B_{-} - B_{-}^{*}\right)\right\} A_{+}^{*} |0\rangle - \alpha^{1/2} \left\{\sinh g(\alpha/2)^{1/2} \left(B_{-} - B_{-}^{*}\right)\right\} A_{-}^{*} |0\rangle, \tag{C.1}$$

where the cosh and sinh are to be represented by their series expansions. From eq. (C.1) we find

$$\begin{aligned} &\widetilde{\phi} |\widetilde{\phi}\rangle = \langle 0| \{\cosh^2 [g(\alpha/2)^{1/2}(B_- B_-^*)] - \alpha \sinh^2 [g(\alpha/2)^{1/2}(B_- B_-^*)] \} | 0 \rangle \\ &= \langle 0| [\{[1 + \cosh g(2\alpha)^{1/2}(B_- B_-^*)]/2\} - \alpha \{[-1 + \cosh g(2\alpha)^{1/2}(B_- B_-^*)]/2\}] | 0 \rangle \end{aligned}$$

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$$= \frac{1}{2}(1+\alpha) + \frac{1}{4}(1-\alpha) \langle 0| \left\{ \exp[g(2\alpha)^{1/2}(B_-B_-^*)] + \exp[-g(2\alpha)^{1/2}(B_-B_-^*)] \right\} | 0 \rangle$$
  
=  $\frac{1}{2}(1+\alpha) + \frac{1}{2}(1-\alpha) \exp(-g^2\alpha),$  (C.2)

where we have used the result that

$$e^{z(B-B^*)} = e^{-zB^*} e^{zB} e^{-\frac{1}{2}z^2}$$
(C.3)  
for boson operators. Using (C.1), we compute  $\langle \widetilde{\phi} | h | \widetilde{\phi} \rangle$  and find, with  $Y = g(\alpha/2)^{1/2}(B_- B_-^*)$ ,  
 $\langle \widetilde{\phi} | h | \widetilde{\phi} \rangle = -|J| \langle 0| [\cosh^2 Y + \alpha \sinh^2 Y] | 0 \rangle + \langle 0| \cosh Y(B_-^*B_-) \cosh Y | 0 \rangle - \alpha \langle 0| \sinh Y(B_-^*B_-) \sinh Y | 0 \rangle$   
 $+ g(\alpha/2)^{1/2} \langle 0| \{\cosh Y(B_- + B_-^*) \sinh Y - \sinh Y(B_- + B_-^*) \cosh Y \} | 0 \rangle$ . (C.4)

Using eq. (C.1), eq. (B.2) and eq. (C.3), we find

$$\widetilde{\widetilde{\epsilon}} = \frac{\langle \widetilde{\phi} | h | \widetilde{\phi} \rangle}{\langle \widetilde{\phi} | \phi \rangle} = -|J| \left[ \frac{(1-\alpha) + (1+\alpha) e^{-g^2 \alpha}}{(1+\alpha) + (1-\alpha) e^{-g^2 \alpha}} \right] - \frac{g^2 \alpha}{2} - \frac{g^2 \alpha (1-\alpha)}{(1+\alpha) + (1-\alpha) e^{-g^2 \alpha}}.$$
(C.5)

The correlation functions can be found using eq. (C.1) and the definitions. We find

$$\langle \widetilde{\widetilde{N}} \rangle = (2/g^2) \langle \widetilde{\phi} | B_-^* B_- | \widetilde{\phi} \rangle / \langle \widetilde{\phi} | \widetilde{\phi} \rangle$$

$$= (2/g^2) \{ \langle 0| (\cosh Y) (B_-^* B_-) (\cosh Y) | 0 \rangle - \alpha \langle 0| (\sinh Y) B_-^* B_- (\sinh Y) | 0 \rangle \} / \langle \widetilde{\phi} | \widetilde{\phi} \rangle$$

$$= (2/g^2) \{ \frac{1}{4} (1-\alpha) \langle 0| e^Y B_-^* B_- e^Y | 0 \rangle + \frac{1}{4} (1-\alpha) \langle 0| e^{-Y} B_-^* B_- e^{-Y} | 0 \rangle + \frac{1}{4} (1+\alpha) \langle 0| e^Y B_-^* B_- e^{-Y} | 0 \rangle$$

$$+ \frac{1}{4} (1+\alpha) \langle 0| e^{-Y} B_-^* B_- e^Y | 0 \rangle \} / \langle \widetilde{\phi} | \widetilde{\phi} \rangle = (2/g^2) \{ \frac{1}{4} (1+\alpha) g^2 \alpha$$

$$- \frac{1}{4} (1-\alpha) g^2 \alpha e^{-g^2 \alpha} \} / \langle \widetilde{\phi} | \widetilde{\phi} \rangle = \alpha \left[ \frac{(1+\alpha) - (1-\alpha) e^{-g^2 \alpha}}{(1+\alpha) + (1-\alpha) e^{-g^2 \alpha}} \right]$$

$$(C.7)$$

and

$$\widetilde{\widetilde{\delta}} = (2^{1/2}g)^{-1} \langle \widetilde{\widetilde{\phi}} | (A_+^*A_- + A_-^*A_+) (B_- + B_-^*) | \widetilde{\widetilde{\phi}} \rangle | \langle \widetilde{\widetilde{\phi}} | \widetilde{\widetilde{\phi}} \rangle$$
  
$$= (2^{1/2}g)^{-1} \alpha^{1/2} | \langle 0 | \{\cosh Y\} (B_- + B_-^*) \sinh Y | 0 \rangle - \langle 0 | \{\sinh Y\} (B_- + B_-^*) \cosh Y | 0 \rangle | \langle \widetilde{\widetilde{\phi}} | \widetilde{\widetilde{\phi}} \rangle$$
  
$$= (2^{1/2}g)^{-1} \alpha | \{ -\frac{1}{2} \langle 0 | e^Y (B_- + B_-^*) e^{-Y} | 0 \rangle + \frac{1}{2} \langle 0 | e^{-Y} (B_- + B_-^*) e^Y | 0 \rangle \} | \langle \widetilde{\widetilde{\phi}} | \widetilde{\widetilde{\phi}} \rangle$$
  
$$= \frac{2\alpha}{(1+\alpha) + (1-\alpha) e^{-g^2\alpha}}. \quad (C.8)$$

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