On the formation and nature of a dipolar Frenkel excitonic insulator

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Abstract. Recently, experiments on expanded fluid mercury, and simulations of alkali metals in liquid ammonia and in molten alkali halides, have motivated interest in the possibility of a Frenkel excitonic insulator (EI) phase. In this paper, we discuss several aspects of a model for describing such a phase. We choose a model Hamiltonian which is the asymptotically exact low-density form for a system of atoms each possessing an sp^3 basis, and present two methods of analysis. The *pairing theory* centres on the broadening of the S → P atomic transition into exciton bands, which, as is known, may lead to the formation of a Frenkel EI phase. We analyse two corrections to the traditional exciton picture: (i) double-excitation processes, which are responsible for the van der Waals stabilization energy, are shown to halve the density predicted for the transition to an EI phase; (ii) correct incorporation of non-boson statistics for the exciton operators is argued to drive the transition from first order to second order. We also analyse the model Hamiltonian via a Hartree approximation, which proves to be the more tractable method, and further allows an explicit description of the EI phase itself. The validity of the Hartree approximation is justified by comparison with the pairing theory.

1. Introduction

In 1963, Knox [1] commented that a new phase might occur in indirect semiconductors if the binding energy of an exciton of the system becomes greater than the single-particle band gap. This new phase, termed an excitonic insulator (EI), would have a ground state containing a macroscopic number of excitons. In subsequent years, several papers were written (see, e.g., [2–5]) on the possible existence of an EI phase constructed from the condensation of Mott–Wannier excitons.

More recently, results from several experiments and simulations have motivated interest in the possible existence of a Frenkel EI phase. Frenkel excitons correspond to the tightly bound, small-radius limit of an exciton, and are generally associated with molecular crystals such as naphthalene and anthracene, or with liquids. The dielectric anomaly observed in expanded fluid mercury [6] has been ascribed to a transition from the low-density insulating phase to a Frenkel EI phase [7–10] in which each mercury atom is associated with a dipole moment, although other explanations have been given [6, 11–13]. Computer simulations of alkali metals in liquid ammonia [14–16] and in molten alkali halides [17] have yielded clear examples of dipolar Frenkel EI phases, with recent experimental support in the latter case [18]. Finally, the formation of a Frenkel EI phase has also been suggested as a possible explanation of the observed properties of a number of solid systems [19–21].

A simple physical picture for the formation of a dipolar Frenkel EI phase may be given along the lines suggested by Logan and Edwards [15, 22]. Consider a system in which the normal ground state of each constituent atom or molecule is a spherically symmetric S state. We suppose that there is a low-lying P state available. Although neither the S state nor the P state possess a dipole moment, a hybrid of these two states does. The atomic dipole moment of this hybrid would polarize its surroundings and the interaction energy between the dipole and its polarized surroundings may be sufficient to overcome the hybridization energy needed to form the dipole in the first place. If this is the case, then a dipolar state in which each atom exists as a hybrid of the normal ground state and an excited state may become the ground state of the system. Logan and Edwards [15, 22] employed results from continuum dielectric theory to estimate the stabilization energy arising from the interaction between a dipolar atom and its polarized surroundings. They concluded that under certain conditions the stabilization energy would be sufficient for the formation of a dipolar Frenkel EI ground state.

Detailed microscopic formulations of the problem have also been given [23–26]. Hall and Wolynes [24, 25] introduced a model in which the instantaneous dipole of an atom occupies discrete vertices of a cube centred on the atom, and pairwise interactions between these dipoles provide the stabilization energy needed for the formation of permanent dipoles. The existence of an EI phase was shown via path integral quantum Monte Carlo simulations of the model system. Xu and Stratt [26] also considered atomic dipoles in a basis consisting of four sp^3 hybrids. Using a path integral representation, they solved the mean spherical approximation for the system and found an EI phase.

The above theories stress the atomic aspect of an EI phase. The dipolar phase is correctly termed an excitonic insulator, since excited atomic states must be mixed into the ground atomic state to form the dipoles. An approach more in keeping, however, with theories of the Mott–Wannier EI phase [2–5] was developed by Turkevich and Cohen [7–10] in their study of the dielectric anomaly observed in mercury [6]. These authors considered the growth with density of the $6^1S_0 \rightarrow 6^1P_1$ transition from a sharp atomic transition to a broad exciton band. When the bottom of the exciton band becomes degenerate with the normal insulating ground state (i.e. when the binding energy of the lowest-energy exciton becomes equal to the single-particle band gap), then the normal insulating phase becomes unstable to the condensation of Frenkel excitons. The broadening of the exciton band may be attributed in part to a dipole–dipole interaction between atoms. We mention also work by Turkevich [27], who ascribed the condensation of Frenkel excitons to the effects of on-site Coulomb interactions between electrons.

In this paper, we present a detailed study of the question of the existence and nature of the Frenkel EI phase. We consider a quantum-mechanical microscopic model of a system of univalent atoms. In section 2, we introduce the model Hamiltonian, and explain how, in principle, this Hamiltonian may give rise to a Frenkel EI phase. We then give a general discussion of two ways in which the model Hamiltonian may be analysed.

The first, which we refer to as the pairing theory, in its simplest form yields the theory of Turkevich and Cohen [7–10]. However, although the latter does give rise to a Frenkel EI phase, it incorporates a number of assumptions that we feel merit a more detailed study. The effects of relaxing these assumptions are presented in section 3. Unfortunately, for technical reasons (the Bogoliubov-like transformation, see section

3.2), we must specialize to a lattice-based system. This is somewhat restrictive, since some of the best candidates for the existence of a Frenkel EI phase occur in the liquid phase. The issues that we wish to address, however, are pertinent to both liquid and solid phases, and are most easily studied in the latter. We therefore leave to a future publication a consideration of the additional features arising from the spatial disorder inherent in the liquid phase.

The second method of analysing the model Hamiltonian, the Hartree approximation, is the subject of section 4. Although the Hartree approximation is, in a sense, less controlled than approximations employed in the pairing theory, it does have a number of advantages. For example, it allows an explicit characterization of the dipolar EI phase, in contrast to the pairing theory, which describes the normal insulating phase and the transition to an EI phase, but not the EI phase itself. Further, the Hartree approximation is applicable to liquid as well as solid phases, although for the sake of comparison with the results of the pairing theory, we again consider the lattice-based system of section 3. In fact, such a comparison shows good agreement between the results of sections 3 and 4 and, we hope, vindicates the use of the Hartree approximation. Finally, in section 5, our conclusions are summarized and some connected issues are discussed.

2. The model Hamiltonian

The model system that we consider consists of a stationary configuration of N atoms, with one valence electron per atom. For the moment, we make no assumption as to whether the atoms form a lattice or are spatially disordered. The valence electrons are described via a tight-binding representation, and we choose as basis states sets of n orbitals centred on each of the N ions (or 'sites'). We assume all basis states to be mutually orthogonal.

We are interested in the possible formation of a Frenkel EI phase, in which the behaviour of the valence electrons leads to each atom acquiring a dipole moment. The optimum conditions for such an EI phase occur in a strongly insulating regime. To this end, we assume that all on-site electron–electron Coulomb terms are sufficiently large that we need only consider electron configurations in which each site is associated with exactly one valence electron, and therefore we take each site to be strictly neutral. Hence, we may neglect all electronic matrix elements that result in a net transfer of electrons between sites. Terms that would involve net electron transfer, such as the one-electron transfer matrix elements, eventually lead to an insulator-to-metal transition, which may compete with the transition to an EI phase. In the present paper, however, we do not consider such a possibility.

With only one electron per site, we need not include any on-site electron–electron terms. Further, with all sites neutral, we may neglect terms associated with charge that occur in a multipole expansion of the intersite Coulomb terms. We thus consider the following model Hamiltonian:

$$H = \sum_{i\alpha} \epsilon_{i\alpha} c^{\dagger}_{i\alpha} c_{i\alpha} - \frac{1}{2} \sum_{\substack{i \neq j \\ \alpha \neq \beta, \gamma \neq \delta}} P^{\alpha\beta,\gamma\delta}_{ij} c^{\dagger}_{i\alpha} c_{i\beta} c^{\dagger}_{j\gamma} c_{j\delta}. \tag{2.1}$$

In equation (2.1), the operator $c^{\dagger}_{i\alpha}$ ($c_{i\alpha}$) creates (annihilates) an electron in the basis state $|i\alpha\rangle$ associated with level α on site i, and the sums run over all N sites and

all n levels. The diagonal term, $\epsilon_{i\alpha}$, is the zero-order site energy of level α on site i. $P_{ij}^{\alpha\beta,\gamma\delta}$ consists of a series of multipole terms, the leading term of which falls off with the separation of two sites as $(\text{separation})^{-3}$, and an exponential exchange-like term. Here, we retain only the leading multipole term:

$$P_{ij}^{\alpha\beta,\gamma\delta} = \langle i\alpha | e(r - R_i) | i\beta \rangle \left(\frac{3(R_j - R_i)(R_j - R_i)}{|R_j - R_i|^5} - \frac{\mathbf{I}}{|R_j - R_i|^3} \right)$$

$$\times \langle j\gamma | e(r - R_j) | j\delta \rangle. \tag{2.2}$$

In equation (2.2), $-e(r - R_i)$ is the dipole moment operator for an electron of charge $-e$ at position r, R_i is the centre-of-mass position of site i, and $\mathbf{I}$ is the identity matrix. This term clearly represents dipolar interactions between sites, and is in fact the second quantized representation of the dipole–dipole interaction considered in [23–26]. $P_{ij}^{\alpha\beta,\gamma\delta}$ satisfies

$$P_{ij}^{\alpha\beta,\gamma\delta} = P_{ji}^{\gamma\delta,\alpha\beta} \tag{2.3}$$

and, if we assume the dipole moment matrix elements to be real, it further follows that

$$P_{ij}^{\alpha\beta,\gamma\delta} = P_{ij}^{\beta\alpha,\gamma\delta} = P_{ij}^{\alpha\beta,\delta\gamma} = P_{ij}^{\beta\alpha,\delta\gamma}. \tag{2.4}$$

In arriving at equation (2.1) for neutral atoms, we have neglected two classes of term. The first involves electron number operators on different sites, and has a leading term of order $O(R^{-5})$, arising from interatomic quadrupole–quadrupole interactions. The second involves an electron number operator on one site and operators for an electronic transition on a second site, and has a leading term of order $O(R^{-4})$, arising from interatomic dipole–quadrupole interactions. Recall that terms in the Hamiltonian involving the overlap matrix of basis states on different sites, and terms involving the transfer of an electron between sites (all of which we have neglected), depend exponentially on the separation of sites. Thus, all terms that have been neglected in constructing the Hamiltonian given by equations (2.1) and (2.2) fall off with the intersite separation faster than $O(R^{-3})$, and Hamiltonian (2.1) may be considered to be the asymptotically exact low-density form.

We now specialize by considering a restricted basis set of one s orbital and three degenerate p orbitals per site. The p orbitals for all sites are spatially quantized along a common set of axes, but we make no assumptions about the orientation of these axes. The Hamiltonian (2.1) becomes

$$H = \sum_i \epsilon_{is} c_{is}^\dagger c_{is} + \sum_{i\alpha} \epsilon_{ip} c_{ip_\alpha}^\dagger c_{ip_\alpha}$$

$$- \frac{1}{2} \sum_{\substack{i \neq j \\ \alpha\beta}} P_{ij}^{sp_\alpha,sp_\beta} (c_{is}^\dagger c_{ip_\alpha} + c_{ip_\alpha}^\dagger c_{is})(c_{js}^\dagger c_{jp_\beta} + c_{jp_\beta}^\dagger c_{js}) \tag{2.5}$$

where Greek letters now refer to the polarization of a p orbital and we have used equation (2.4).

The first line of equation (2.5) gives the Hamiltonian for a collection of isolated four-level atoms. For an isolated atom with a single valence electron, population of the p levels is obviously energetically unfavourable owing to the fact that $\epsilon_{ip} > \epsilon_{is}$. In the bulk phase, however, excitation to a p level may be stabilized by the dipolar terms in the second line of equation (2.5), and it is this feature that is responsible for the possible formation of an EI phase. The magnitude of the dipolar matrix elements in the second line of equation (2.5) increases with decreasing intersite separation, i.e. with increasing density. Therefore, we expect a transition to an EI phase, if it does occur, to occur as the density is increased. We must bear in mind, however, that it is possible that the density at which the transition is predicted to occur is outside the range of validity of the low-density form of the Hamiltonian that we have used. One simple way to correct for deviations from the low-density form of the Hamiltonian is to replace the dipolar form of equation (2.2) by a more general form, taken, for example, from detailed spectroscopic calculations [10].

Before discussing practical methods for analysing the behaviour of Hamiltonian (2.5), we make some general comments. The total N-electron wavefunction of the system (for the ground state or any excited state) may be expanded in terms of the basis set of all allowed electronic configurations of the N electrons. One may classify possible electronic configurations according to the number of excited sites, i.e. the number of sites for which the valence electron is in a p-level state. In this context, there are two distinct types of term in the second line of equation (2.5). First, there are those which excite an electron on site i from the s level to a p level and relax an electron on site j from a p level to the s level, or *vice versa*, and thus preserve the total number of excited sites. Secondly, there are *double-excitation* terms, which either excite electrons on both sites i and j or relax electrons on both sites i and j, and thus change the total number of excited sites by two. It follows that, in ordinary circumstances, the total N-electron wavefunction of the system consists either solely of electronic configurations with even numbers of excited sites or solely configurations with odd numbers of excited sites. In particular, the normal ground state (i.e. in the absence of an EI phase) consists not only of the configuration with no excited sites, but also configurations with two, four, ... excited sites.

There are two important points associated with this observation. First, mixing with doubly, quadruply, ... excited configurations means that the ground-state energy decreases as the density of the system increases; this is the origin of the van der Waals binding energy (see section 3.2). Secondly, since the site dipole moment operator connects configurations differing solely by one in the number of excited sites, none of the wavefunctions described above possesses dipolar sites.

In fact, a dipolar ground state *is* attainable within this picture. If an excited state consisting of odd configurations becomes degenerate with the ground state, which itself consists of even configurations, then only an infinitesimal perturbation (such as an arbitrarily weak electric field) is required to mix these states. The ground state then distorts so that it is a mixture of even and odd configurations, and thus possesses dipolar sites. In other words, a transition to a dipolar ground state (the EI phase) is deemed to occur when an excited state consisting of odd configurations becomes degenerate with the ground state. This is the criterion for the transition to a dipolar Frenkel EI phase that we use in section 3.

We now describe two approaches to the analysis of Hamiltonian (2.5). The first, and most common, method (which we shall refer to as the *pairing theory*) is to group

the electron (Fermi) operators into pairs, defining

$$b_{i\alpha} = c_{is}^\dagger c_{ip_\alpha} \qquad b_{i\alpha}^\dagger = c_{ip_\alpha}^\dagger c_{is}. \qquad (2.6)$$

With these definitions, and defining the zero of energy to be such that all electrons are in s levels ($\sum_i \epsilon_{is} = 0$), equation (2.5) reduces to

$$H = \sum_{i\alpha} \Delta \epsilon_i b_{i\alpha}^\dagger b_{i\alpha} - \frac{1}{2} \sum_{\substack{i \neq j \\ \alpha\beta}} P_{ij}^{sp_\alpha,sp_\beta} (b_{i\alpha}^\dagger + b_{i\alpha})(b_{j\beta}^\dagger + b_{j\beta}) \qquad (2.7)$$

where $\Delta \epsilon_i = \epsilon_{ip} - \epsilon_{is}$. The operators $b_{i\alpha}^\dagger / b_{i\alpha}$ obey neither Fermi–Dirac nor Bose–Einstein statistics (see section 3.3), except in the limit of a vanishing concentration of excitations whence the commutation relations reduce to those applicable to bosons.

To bring Hamiltonian (2.7) into a tractable form, three approximations are generally made. First, the cross-terms in the off-diagonal part of the Hamiltonian, for which $\alpha \neq \beta$, are neglected. Secondly, the double-excitation terms in the off-diagonal part of the Hamiltonian are also neglected. Finally, the operators $b_{i\alpha}^\dagger / b_{i\alpha}$ are generally assumed to obey Bose–Einstein statistics. With these approximations, the Hamiltonian (2.7) separates into three single-band tight-binding Hamiltonians:

$$H = \sum_\alpha \left(\sum_i \Delta \epsilon_i b_{i\alpha}^\dagger b_{i\alpha} - \sum_{i \neq j} P_{ij}^{sp_\alpha,sp_\alpha} b_{i\alpha}^\dagger b_{j\alpha} \right). \qquad (2.8)$$

Hamiltonians of this simple form have been the basis of much work on excitons, from the early work of Heller and Marcus [28] through to the more recent work of Turkevich and Cohen [7–10]. (We should also add that a term describing so-called *dynamic interaction* between excitons is often added to the above Hamiltonian. If this term is attractive, then it may lead to the formation of biexcitons, polyexcitons or a liquid of excitons [29–31]. We do not consider such interactions in the present work.)

The Hamiltonian (2.8) is sufficient to predict a transition to an EI phase, but the question arises: To what extent are the approximations leading to equation (2.8) valid, in this context? The neglected cross-terms connect excitations of one polarization with those of a different polarization. It is straightforward to show (see section 3.1) that for the EI phase of primitive cubic lattices, at least, this interaction between different polarizations does indeed vanish (assuming boson statistics). The cross-terms may, however, be important for other lattices and disordered systems. The neglected double-excitation terms are associated with the same matrix element as the off-diagonal terms that are retained. They can, though, be neglected at very low densities, since they connect states separated in energy by $\Delta \epsilon_i + \Delta \epsilon_j$, in contrast to the retained terms, which connect states separated in energy by $\Delta \epsilon_i - \Delta \epsilon_j$. As explained above, however, the transition to an EI phase occurs at a higher density such that banding leads to states with different numbers of excited sites becoming degenerate. The double-excitation terms, which connect states differing by two in the number of excited sites, must surely then be important. Lastly, the assumption of Bose–Einstein statistics is valid only for a vanishingly small concentration of excitations. Since the ground state of an EI phase must consist of a macroscopic concentration of excitations,

the assumption of boson statistics is certainly not valid within this phase, and may or may not be valid in the normal non-dipolar phase as the transition is approached. Thus, these approximations would seem worthy of further investigation. In section 3, we consider the neglect of the double-excitation terms and the assumption of boson statistics in more detail.

The alternative method of analysing Hamiltonian (2.5) is to perform a Hartree decoupling on the terms quartic in the electronic operators. (In fact, since the model Hamiltonian contains no exchange terms, this may also be considered a Hartree–Fock decoupling.) One thus makes the following type of approximation:

$$c_{is}^\dagger c_{ip_\alpha} c_{js}^\dagger c_{jp_\beta} \simeq c_{is}^\dagger c_{ip_\alpha} \langle c_{js}^\dagger c_{jp_\beta}\rangle + \langle c_{is}^\dagger c_{ip_\alpha}\rangle c_{js}^\dagger c_{jp_\beta} - \langle c_{is}^\dagger c_{ip_\alpha}\rangle\langle c_{js}^\dagger c_{jp_\beta}\rangle \qquad (2.9)$$

where $\langle \ldots \rangle$ denotes a quantum-mechanical average over the trial Hartree wavefunction. With this approximation, and using equation (2.3), equation (2.5) reduces to

$$H = \sum_{i\alpha}\Delta\epsilon_i\, c_{ip_\alpha}^\dagger c_{ip_\alpha} - \sum_{\substack{i\neq j\\ \alpha\beta}} P_{ij}^{sp_\alpha,sp_\beta}(\langle c_{js}^\dagger c_{jp_\beta}\rangle + \langle c_{jp_\beta}^\dagger c_{js}\rangle)(c_{is}^\dagger c_{ip_\alpha} + c_{ip_\alpha}^\dagger c_{is})$$

$$+ \frac{1}{2}\sum_{\substack{i\neq j\\ \alpha\beta}} P_{ij}^{sp_\alpha,sp_\beta}(\langle c_{is}^\dagger c_{ip_\alpha}\rangle + \langle c_{ip_\alpha}^\dagger c_{is}\rangle)(\langle c_{js}^\dagger c_{jp_\beta}\rangle + \langle c_{jp_\beta}^\dagger c_{js}\rangle). \quad (2.10)$$

We have again defined the zero of energy to be such that all electrons are in s levels.

The last term of equation (2.10) contributes to the total energy, but not to the quantum mechanics, of the system. The remaining (quantum-mechanical) terms describe an effective one-electron problem, which is straightforward to solve. In fact, equation (2.10) clearly separates into N atomic Hamiltonians, with matrix elements for a particular site depending on the expectation values of operators on all other sites. Thus, what is required is a self-consistent solution of a four-level atomic Hamiltonian. This solution is presented in section 4.

The Hartree approximation is the simplest way of analysing the model Hamiltonian; and further, in contrast to the pairing theory, it provides information on the dipolar state itself. It is not, however, obvious *a priori* how reliable the Hartree approximation (2.9) may be expected to be. In section 4, we solve the Hartree equations for an infinite system, and find good agreement with many of the results of the pairing theory given in section 3. As a counter-example, in section 5 we show that the Hartree equations would also predict an EI phase in a two-site system, for which an exact analysis shows that there is no such phase.

3. Pairing theory

We now study in detail the version of the model Hamiltonian given in equation (2.7). In this approach, the Hamiltonian is expressed in terms of the operators $b_{i\alpha}^\dagger/b_{i\alpha}$, which are defined, via equation (2.6), in terms of pairs of electron operators. As discussed in the previous section, the aim is to assess the validity of two of the three approximations used in deriving the simpler Hamiltonian (2.8), viz. the neglect of the double-excitation terms and the assumption of Bose–Einstein statistics. Particular

attention will be paid to the implications for the predicted existence and nature of a Frenkel EI phase. To this end, it is expedient to select a very simple example: an infinite Bravais lattice with $\Delta\epsilon_i = \Delta\epsilon$ for all i.

Retaining the approximation (upon which we comment further below) of neglecting the cross-terms in the second term on the right-hand side of equation (2.7), for which $\alpha \neq \beta$, we thus study the Hamiltonian

$$H = \sum_{\alpha} \left(\sum_{i} \Delta\epsilon \, b_{i\alpha}^{\dagger} b_{i\alpha} - \frac{1}{2} \sum_{i \neq j} P_{ij}^{\text{sp}_\alpha, \text{sp}_\alpha} (b_{i\alpha}^{\dagger} + b_{i\alpha})(b_{j\alpha}^{\dagger} + b_{j\alpha}) \right) \tag{3.1}$$

where the sums are over all N ($N \to \infty$) sites on the lattice. The Hamiltonian (3.1) includes the double-excitation terms; and the operators do not, in general, obey boson statistics. It is the effects of these two factors that we wish to investigate, but first, for the sake of comparison, we consider the simpler case in which the double-excitation terms are neglected and the operators are assumed to obey boson statistics.

3.1. No double-excitation terms, boson statistics

Neglecting double-excitation terms, equation (3.1) reduces to

$$H = \sum_{\alpha} \left(\sum_{i} \Delta\epsilon \, b_{i\alpha}^{\dagger} b_{i\alpha} - \sum_{i \neq j} P_{ij}^{\text{sp}_\alpha, \text{sp}_\alpha} b_{i\alpha}^{\dagger} b_{j\alpha} \right) \tag{3.2}$$

and the operators $b_{i\alpha}^{\dagger} / b_{i\alpha}$ are now assumed to obey boson statistics, a fact that we have used in simplifying the second term on the right-hand side. Equation (3.2) is identical to equation (2.8) for the special case of an infinite Bravais lattice with constant $\Delta\epsilon_i$.

The Hamiltonian (3.2) is diagonalized by introducing the operator $b_{k\alpha}$ and its Hermitian conjugate $b_{k\alpha}^{\dagger}$, defined via

$$b_{i\alpha} = \frac{1}{\sqrt{N}} \sum_{k} e^{ik \cdot R_i} b_{k\alpha} \qquad b_{i\alpha}^{\dagger} = \frac{1}{\sqrt{N}} \sum_{k} e^{-ik \cdot R_i} b_{k\alpha}^{\dagger} \tag{3.3}$$

where the sum is over the first Brillouin zone. It is straightforward to show that the transformation to the operators, $b_{k\alpha}$, is canonical, so that the commutation properties of the original operators (in this case of Bose–Einstein form) are preserved. With the substitutions (3.3), equation (3.2) reduces to

$$H = \sum_{k\alpha} \left[\Delta\epsilon - \rho M^2 D^{\alpha\alpha}(k) \right] b_{k\alpha}^{\dagger} b_{k\alpha}. \tag{3.4}$$

Here, ρ is the number density of lattice sites, $M = \langle is | e(r - R_i)_\alpha | ip_\alpha \rangle$ (for any α) is the transition dipole moment, and

$$D^{\alpha\alpha}(k) = (\rho M^2)^{-1} \sum_{\delta \neq 0} P_{\delta}^{\text{sp}_\alpha, \text{sp}_\alpha} e^{ik \cdot \delta} \tag{3.5}$$

$$D^{\alpha\alpha}(k) = D^{\alpha\alpha}(-k) \qquad \sum_{k} D^{\alpha\alpha}(k) = 0 \tag{3.6}$$

where the sum in equation (3.5) is over all non-zero separations between lattice sites.

We define the vacuum state of the system, $|0\rangle$, to be such that $b_{k\alpha}|0\rangle = 0$ and $\langle 0|0\rangle = 1$; hence, it is the state for which all electrons occupy s levels. Relative to this vacuum state, the Hamiltonian (3.4) possesses the single-exciton eigenstates

$$b_{k\alpha}^{\dagger}|0\rangle \tag{3.7}$$

with eigenenergies

$$E_{k\alpha} = \Delta\epsilon - \rho M^2 D^{\alpha\alpha}(k). \tag{3.8}$$

The many-exciton state

$$b_{k\alpha}^{\dagger} b_{k'\alpha'}^{\dagger} \dots |0\rangle \tag{3.9}$$

is also an eigenstate of the system, and has an energy

$$E_{k\alpha} + E_{k'\alpha'} + \cdots. \tag{3.10}$$

This is the traditional solution to the Frenkel exciton problem [28, 32]. Equation (3.8) describes the energies of a band of single-exciton states. These energies depend on the lattice sums given in equation (3.5), and the sums may be evaluated by noting that $D^{\alpha\alpha}(k)$ is precisely the quantity '$D^{ii}(k)$' defined by Cohen and Keffer in equation (16) of [33]. Cohen and Keffer [33] describe the properties of these sums for simple cubic (SC), face-centred cubic (FCC) and body-centred cubic (BCC) lattices, and give tables from which $D^{\alpha\alpha}(k)$ may be calculated for a selection of points in the first Brillouin zone. The single-exciton states occupy an energy band that broadens linearly with density, as indicated in equation (3.8). This band is well behaved except near $k = 0$, where $D^{\alpha\alpha}(k)$ is only piecewise continuous, splitting into transverse and longitudinal branches. (Note that, for a large but finite lattice, the above behaviour is modified in a small region about $k = 0$ [33].)

The behaviour of the many-exciton system follows straightforwardly, and is shown schematically in figure 1. At sufficiently low densities, the ground state is the zero-exciton vacuum state, which has a constant energy of zero. Above this, there is a band of single-exciton states with energies given by equation (3.8), and at higher energies there are bands associated with two, three, . . . excitons. Because we have neglected the double-excitation terms in the Hamiltonian, the number of excited sites is a good quantum number and a band of n-exciton states is associated with electronic configurations containing n excited sites.

As the density is increased, the single- and many-exciton bands broaden and the energy gap between these excited states and the ground state decreases. At a critical density, ρ_c, such that $E_{k\alpha} = 0$ for the lowest-energy single-exciton state, the lower edges of the single-exciton band and all the many-exciton bands become simultaneously degenerate with the ground state. At this point, there is mixing between the ground state and the single- and many-exciton states leading to a dipolar state, as described in section 2. Since there is mixing with all many-exciton bands, one would expect the condensation of a macroscopic number of excitons. Within this
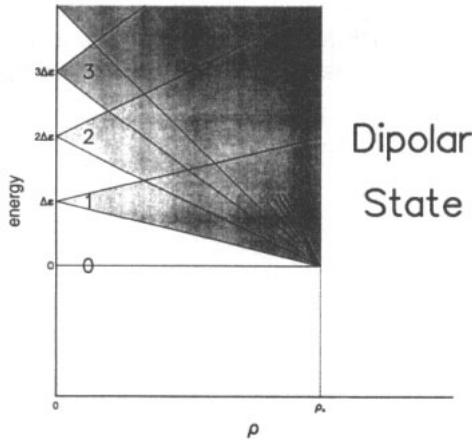
Figure 1. A schematic illustration of the exciton bands derived from equations (3.8) and (3.10) as a function of density, for the case where double-excitation terms in the Hamiltonian are neglected and boson statistics assumed. The bands are labelled according to the number of excitons, or equivalently the number of excited sites, contributing to the many-exciton states. At the critical density, ρ_c, the lower edges of all m-exciton bands ($m \geqslant 1$) become simultaneously degenerate with the ground state, and for densities $\rho > \rho_c$ there is a dipolar Frenkel EI phase.
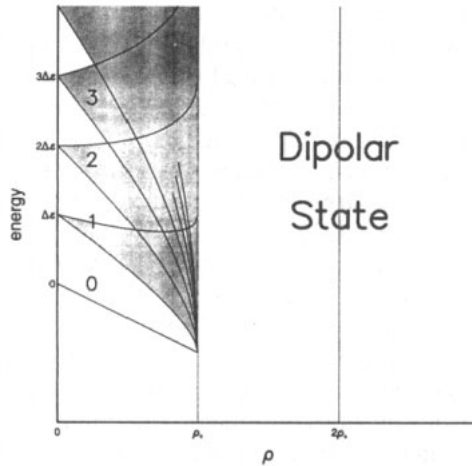

Figure 2. A schematic illustration of the renormalized exciton bands derived from equations (3.20) and (3.22) as a function of density, for the case where double-excitation terms in the Hamiltonian are retained and boson statistics assumed. The bands are labelled according to the number of renormalized excitons contributing to the many-renormalized-exciton states. Note that the expectation value of the number of excited sites is macroscopically large for all states. At the critical density, ρ_c, the lower edges of all m-renormalized exciton bands ($m \geqslant 1$) become simultaneously degenerate with the ground state, and for densities $\rho > \rho_c$ there is a dipolar Frenkel EI phase. The vertical line at the density $2\rho_c$ indicates where the transition to a dipolar Frenkel EI phase would occur if the double-excitation terms in the Hamiltonian were neglected.

model Hamiltonian, we would thus anticipate a first-order transition to an EI phase when $\Delta\epsilon - \rho M^2 D^{\alpha\alpha}(k)$ first becomes zero for some value of k, i.e.

$$\rho_c = \frac{\Delta\epsilon}{M^2 D^{\alpha\alpha}(k)} \tag{3.11}$$

where k is that appropriate to the lowest-energy exciton.

For FCC and BCC lattices, the state associated with the lower edge of the single-exciton band, and consequently with the lower edges of all many-exciton bands, is the transverse $k = 0$ exciton. There is thus a transition to a dipolar state when the transverse $k = 0$ exciton becomes degenerate with the ground state. Assuming that the dipolar state reflects the translational symmetry of the $k = 0$ exciton, one therefore expects the dipolar state to be ferroelectric. In contrast, if one follows a similar argument for a simple cubic lattice, then one predicts an antiferroelectric dipolar state in which the dipoles are ferroelectrically aligned parallel to the axis of polarization, but antiferroelectrically aligned perpendicular to the axis of polarization.

The cross-terms that were neglected in deriving equation (3.1) lead to terms in $D^{\alpha\beta}(k)$ ($\alpha \neq \beta$), defined by analogy with equation (3.5). If, for a cubic lattice, we choose the orientation of the p orbitals to be such that we may realize a transverse $k = 0$ exciton, then the quantities $D^{\alpha\beta}(0)$ vanish [32, 33]. Thus, we would expect the neglected cross-terms to have no effect for cubic lattices that exhibit a ferroelectric EI phase, i.e. the FCC and BCC lattices. The cross-terms also vanish for the wavevector associated with the transition to an EI phase in a simple cubic lattice [33]. Thus, although the cross-terms are in general non-zero, for the three primitive cubic lattices the cross-terms should not affect the transition to the EI phase.

The scenario leading to equation (3.11) is essentially that considered by Turkevich and Cohen [7–10] in their investigation of the possible Frenkel EI phase in expanded fluid mercury. Replacing the quantities $P_{ij}^{\text{sp}_\alpha,\text{sp}_\alpha}$ by matrix elements taken from spectroscopic calculations, they predicted [10] a transition to an EI phase at a density close to the observed dielectric anomaly [6].

3.2. Double-excitation terms, boson statistics

We next consider the effect of reintroducing the double-excitation terms. We therefore return to equation (3.1) but, for the moment, retain the approximation of assuming boson statistics for the operators $b_{i\alpha}^\dagger / b_{i\alpha}$. Performing the canonical transformation (3.3), and using equations (3.6), we find

$$H = \sum_{k\alpha} [\Delta\epsilon - \rho M^2 D^{\alpha\alpha}(k)] b_{k\alpha}^\dagger b_{k\alpha} - \frac{\rho M^2}{2} \sum_{k\alpha} D^{\alpha\alpha}(k)(b_{k\alpha}^\dagger b_{-k\alpha}^\dagger + b_{k\alpha} b_{-k\alpha}).$$

$$\tag{3.12}$$

In addition to the terms occurring in Hamiltonian (3.4), equation (3.12) includes off-diagonal elements connecting exciton states of wavevector k with states of wavevector $-k$. Such a situation is reminiscent of the BCS (Bardeen–Cooper–Schrieffer) Hamiltonian of superconductivity theory, which is diagonalized via the so-called Bogoliubov transformation. Here, we employ a related canonical transformation [34], which differs slightly from the Bogoliubov transformation in order to take into account the boson nature of the operators.

We define new operators, $B_{k\alpha}$ and $B_{k\alpha}^{\dagger}$, via

$$b_{k\alpha} = (\cosh\theta_{k\alpha})B_{k\alpha} - (\sinh\theta_{k\alpha})B_{-k\alpha}^{\dagger}$$

$$b_{k\alpha}^{\dagger} = (\cosh\theta_{k\alpha})B_{k\alpha}^{\dagger} - (\sinh\theta_{k\alpha})B_{-k\alpha} \qquad (3.13)$$

with

$$\theta_{k\alpha} = \theta_{-k\alpha} = \theta_{k\alpha}^{*} \qquad (3.14)$$

where $\theta_{k\alpha}$ is a parameter that we are free to choose. With these definitions, and using equations (3.6) and (3.14) together with the boson properties of the operators to simplify the resulting expression, equation (3.12) reduces to

$$H = \sum_{k\alpha}[\{[\Delta\epsilon - \rho M^{2}D^{\alpha\alpha}(k)]\cosh(2\theta_{k\alpha}) + \rho M^{2}D^{\alpha\alpha}(k)\sinh(2\theta_{k\alpha})\}B_{k\alpha}^{\dagger}B_{k\alpha}$$

$$-\tfrac{1}{2}\{[\Delta\epsilon - \rho M^{2}D^{\alpha\alpha}(k)]\sinh(2\theta_{k\alpha}) + \rho M^{2}D^{\alpha\alpha}(k)\cosh(2\theta_{k\alpha})\}$$

$$\times (B_{k\alpha}^{\dagger}B_{-k\alpha}^{\dagger} + B_{k\alpha}B_{-k\alpha}) + \tfrac{1}{2}\{[\Delta\epsilon - \rho M^{2}D^{\alpha\alpha}(k)]\cosh(2\theta_{k\alpha})$$

$$+ \rho M^{2}D^{\alpha\alpha}(k)\sinh(2\theta_{k\alpha}) - \Delta\epsilon\}]. \qquad (3.15)$$

The coefficient of the double-excitation terms in equation (3.15) is made zero by choosing the parameter $\theta_{k\alpha}$ such that

$$\tanh(2\theta_{k\alpha}) = \frac{-\rho M^{2}D^{\alpha\alpha}(k)}{\Delta\epsilon - \rho M^{2}D^{\alpha\alpha}(k)}. \qquad (3.16)$$

It follows from equation (3.16) that

$$\sinh(2\theta_{k\alpha}) = \frac{-\rho M^{2}D^{\alpha\alpha}(k)}{\{[\Delta\epsilon - \rho M^{2}D^{\alpha\alpha}(k)]^{2} - [\rho M^{2}D^{\alpha\alpha}(k)]^{2}\}^{1/2}}$$

$$\cosh(2\theta_{k\alpha}) = \frac{\Delta\epsilon - \rho M^{2}D^{\alpha\alpha}(k)}{\{[\Delta\epsilon - \rho M^{2}D^{\alpha\alpha}(k)]^{2} - [\rho M^{2}D^{\alpha\alpha}(k)]^{2}\}^{1/2}}. \qquad (3.17)$$

With these substitutions, the remaining terms of equation (3.15) yield

$$H = \sum_{k\alpha}\{[\Delta\epsilon - \rho M^{2}D^{\alpha\alpha}(k)]^{2} - [\rho M^{2}D^{\alpha\alpha}(k)]^{2}\}^{1/2}(B_{k\alpha}^{\dagger}B_{k\alpha} + \tfrac{1}{2}) - \tfrac{3}{2}N\Delta\epsilon. \qquad (3.18)$$

We redefine the vacuum state of the system, $|0\rangle$, to be such that $B_{k\alpha}|0\rangle = 0$ and $\langle 0|0\rangle = 1$. Relative to this vacuum state, the Hamiltonian (3.18) possesses the single-particle eigenstates

$$B_{k\alpha}^{\dagger}|0\rangle \qquad (3.19)$$

with eigenenergies

$$\tilde{E}_{k\alpha} = \{[\Delta\epsilon - \rho M^2 D^{\alpha\alpha}(k)]^2 - [\rho M^2 D^{\alpha\alpha}(k)]^2\}^{1/2}. \tag{3.20}$$

To distinguish these states from the exciton states defined by equation (3.7), we use the name *renormalized excitons*. The many-renormalized-exciton state

$$B_{k\alpha}^{\dagger} B_{k'\alpha'}^{\dagger} \dots |0\rangle \tag{3.21}$$

is also an eigenstate of the system, and has an energy

$$\tilde{E}_{k\alpha} + \tilde{E}_{k'\alpha'} + \cdots. \tag{3.22}$$

Although the number of renormalized excitons is a good quantum number, the number of bare excitons (or equivalently the number of excited sites) is no longer a good quantum number. This is obvious from the presence of the double-excitation terms, which do not conserve the number of excited sites, and follows formally from the fact that the operator for the number of excitons, $b_{k\alpha}^{\dagger} b_{k\alpha}$, does not commute with the Hamiltonian (3.18).

We may, however, calculate the expectation value of the number of excitons, or equivalently the expectation value of the number of excited sites. For example, the expectation value of the number of excitons per site in the vacuum state, $|0\rangle$, is given by

$$\langle n \rangle_{(0)}^{\text{bos}} \equiv \frac{1}{N} \sum_{i\alpha} \langle 0|b_{i\alpha}^{\dagger} b_{i\alpha}|0\rangle = \frac{1}{N} \sum_{k\alpha} \langle 0|b_{k\alpha}^{\dagger} b_{k\alpha}|0\rangle = \frac{1}{N} \sum_{k\alpha} \sinh^2 \theta_{k\alpha}$$

$$= \frac{1}{2N} \sum_{k\alpha} \left(\frac{\Delta\epsilon - \rho M^2 D^{\alpha\alpha}(k)}{\{[\Delta\epsilon - \rho M^2 D^{\alpha\alpha}(k)]^2 - [\rho M^2 D^{\alpha\alpha}(k)]^2\}^{1/2}} - 1 \right). \tag{3.23}$$

In deriving the third equality of equation (3.23) we have used the fact that $B_{k\alpha}$ destroys the vacuum state, and in deriving the last line we have used equation (3.17). Thus, the number of excitons or excited sites in the vacuum state increases from zero as the density increases. For a system with a finite number of sites and periodic boundary conditions, $\langle n \rangle_{(0)}^{\text{bos}}$ clearly diverges as $\rho \to \Delta\epsilon/2M^2 D^{\alpha\alpha}(k)$ for the particular wavevector corresponding to the largest $D^{\alpha\alpha}(k)$ (which, as we shall see below, is the density ρ_c of the transition to an EI phase). For an infinite system, however, this divergence is integrable and $\langle n \rangle_{(0)}^{\text{bos}}$ remains finite. For example, $\langle n \rangle_{(0)}^{\text{bos}} = 0.086$ for an FCC lattice at the transition density. Since we have calculated the number of excitons per site, it is clear that for densities $0 < \rho < \rho_c$ the vacuum state possesses a macroscopic number of excited sites.

At sufficiently low densities, the vacuum state is the ground state of the system. From equation (3.18), the ground-state energy per site is then

$$E_{(0)}^{\text{bos}} = \frac{1}{2N} \sum_{k\alpha} [\{[\Delta\epsilon - \rho M^2 D^{\alpha\alpha}(k)]^2 - [\rho M^2 D^{\alpha\alpha}(k)]^2\}^{1/2} - \Delta\epsilon]. \tag{3.24}$$

In the limit of zero density, the ground-state energy is clearly zero, as required; but at finite density, the ground-state energy is negative and decreases with increasing density. This energy is clearly an extensive property, and may be associated with the van der Waals stabilization energy of a molecular system [35]. The stabilization is a consequence of the double-excitation terms, which mix into the zero-exciton state (which has all electrons in an s state) states with two, four, ... excitations. In fact, the ground state is associated with an extensive number of excited sites, as may be seen from equation (3.23).

Directly above the ground state lies a band of single-renormalized-exciton states, with energies above that of the ground state given by equation (3.20). The energy of a renormalized exciton of wavevector k and polarization α is clearly different from that of the corresponding simple exciton, but nevertheless the renormalized exciton states are ordered in energy in the same way as the exciton states described in the previous section; i.e. if the bottom of an exciton band is associated with a transverse $k = 0$ state, then so is the bottom of the renormalized exciton band. At higher energies, there are further bands associated with two, three, ... renormalized excitons (see figure 2).

At very low densities, the above picture reduces to that described in section 3.1. This may be seen as follows. Expanding the square root in equation (3.20) to linear order in ρ, equation (3.20) reduces to equation (3.8). Further, to linear order in ρ, the ground-state energy given by equation (3.24) is zero, and the operator $B_{k\alpha}$ is identical to the operator $b_{k\alpha}$. Thus, the first deviation from the simple picture of section 3.1 arises from terms of order $O(\rho^2)$. Such high-order correction terms may not be necessary for spectroscopic applications, but are certainly important for the density regime in which an EI transition occurs.

A transition to an EI state occurs in the same way as for the simpler model of section 3.1. As the density is increased, the single- and many-renormalized exciton bands broaden (see figure 2), giving a first-order transition to an EI phase when the lower edges of these bands become simultaneously degenerate with the ground state. The critical density, ρ_c, for the transition is the density at which $\bar{E}_{k\alpha}$, as given by equation (3.20), is first zero for some value of k i.e.

$$\rho_c = \frac{\Delta\epsilon}{2M^2 D^{\alpha\alpha}(k)} \tag{3.25}$$

where k is that appropriate to the lowest-energy renormalized exciton. *Comparison with equation (3.11) shows that addition of the double-excitation terms halves the density predicted for the transition.* Since the renormalized exciton states are ordered in energy in the same way as the bare exciton states, the ferroelectric or antiferroelectric nature of the dipolar EI phase is the same as that predicted by the analysis of section 3.1.

Finally, we reiterate that for densities $0 < \rho < \rho_c$, the ground state, although non-dipolar, does contain a non-zero fraction of excited sites (of the order of 10%, see discussion following equation (3.23)). Thus, any analysis that measures the number of excited sites would show a slow increase in this quantity for densities $0 < \rho < \rho_c$, followed by a discontinuous rise at $\rho = \rho_c$. As will become more apparent when we consider non-boson statistics, it is the site dipole moment, rather than the number of excited sites, that is the appropriate order parameter for this transition.

3.3. No double-excitation terms, correct statistics

We now return to the simpler Hamiltonian considered in section 3.1, and relax the

assumption of boson statistics. From the fermion nature of the electron operators, it is straightforward to show that the operators defined by equation (2.6) obey the following commutation relations:

$$[b_{i\alpha}, b_{j\beta}] = [b^\dagger_{i\alpha}, b^\dagger_{j\beta}] = 0 \tag{3.26}$$

$$[b_{i\alpha}, b^\dagger_{j\beta}] = \delta_{ij}(\delta_{\alpha\beta}c^\dagger_{is}c_{is} - c^\dagger_{ip_\beta}c_{ip_\alpha}). \tag{3.27}$$

These operators clearly do not, in general, obey boson statistics, as was assumed in the preceding sections. If one restricts the model to only one polarization α (as is usually done, see e.g. [28, 36]), then the operators in fact obey Pauli statistics, i.e. operators referring to the same site satisfy fermion anticommutation relations while operators referring to different sites satisfy boson commutation relations. The above relations do, however, reduce to those appropriate to bosons when the operators act on a state of zero exciton density—in that case, $c^\dagger_{is}c_{is}$ yields one and $c^\dagger_{ip_\beta}c_{ip_\alpha}$ yields zero for all sites. The boson approximation is thus expected to be reasonable for small densities of excitons.

The boson approximation does, however, break down for high densities of excitons, such as those produced by powerful lasers [37, 38]. In the present context, an EI phase is associated with a macroscopic number of excitons and so corrections to a boson description may well be important in the approach to such a phase. It is, therefore, of interest to take into account the correct statistics of the operators $b^\dagger_{i\alpha}/b_{i\alpha}$. One method of tackling this problem is to transform to a set of operators that rigorously obey Bose–Einstein statistics. Such a transformation was proposed by Agranovich and Tošić [29] (see also [39, 40]), who related the exciton operator to an infinite series of boson operators. Retaining only the first term in this series, one recovers the boson approximation of section 3.1. If one further includes the second term, then a transformation of Anderson [34] (see also [41]) is recovered. Both the transformation due to Agranovich and Tošić [29] and that due to Anderson [34] lead to additional terms in the Hamiltonian that describe the so-called *kinematic interaction* between the bosons. Physically, these terms account for scattering processes between excitons which arise because a site, which may contribute to two or more exciton states, can only be singly excited.

In the present paper, however, we follow Kaplan [36] and do not make such a transformation; instead we deal directly with the non-boson operators, $b^\dagger_{i\alpha}/b_{i\alpha}$. It follows from the commutation relations given in equations (3.26) and (3.27) that the exciton operators, defined via equation (3.3), obey the relations

$$[b_{k\alpha}, b_{k'\beta}] = [b^\dagger_{k\alpha}, b^\dagger_{k'\beta}] = 0 \tag{3.28}$$

$$[b_{k\alpha}, b^\dagger_{k'\beta}] = \frac{1}{N}\sum_i e^{i(k'-k)\cdot R_i}(\delta_{\alpha\beta}c^\dagger_{is}c_{is} - c^\dagger_{ip_\beta}c_{ip_\alpha}). \tag{3.29}$$

Note that the transformation (3.3) is not canonical, as it was when boson statistics were assumed for the operators $b^\dagger_{i\alpha}/b_{i\alpha}$, since the commutation relation (3.29) differs from the relation (3.27).

Neglecting double-excitation terms, the Hamiltonian of interest is given by equation (3.2), where the operators $b^\dagger_{i\alpha}/b_{i\alpha}$ now obey the commutation relations (3.26)

and (3.27). Performing the transformation (3.3), and taking into account the second relation of equation (3.6), the Hamiltonian again reduces to equation (3.4). It must be stressed, however, that with the statistics implied by equations (3.28) and (3.29), $b_{k\alpha}^{\dagger} b_{k\alpha}$ is not the number operator for the number of excitons of wavevector k and polarization α [36].

Taking the vacuum state, $|0\rangle$, to be as defined in section 3.1 (i.e. such that it is destroyed by $b_{k\alpha}$), we see immediately that it is again of constant and zero energy. Consider next the Hamiltonian (3.4) acting on the single-exciton state given by equation (3.7). Using equation (3.29) and the fact that $b_{k\alpha}$ destroys the vacuum state, we have

$$H\, b_{k\alpha}^{\dagger}|0\rangle = \sum_{k'\beta}[\Delta\epsilon - \rho M^2 D^{\beta\beta}(k')]b_{k'\beta}^{\dagger}\left(\frac{1}{N}\sum_{i}\mathrm{e}^{\mathrm{i}(k-k')\cdot R_i}(\delta_{\alpha\beta}c_{is}^{\dagger}c_{is} - c_{ip_\alpha}^{\dagger}c_{ip_\beta})\right)|0\rangle$$

$$= [\Delta\epsilon - \rho M^2 D^{\alpha\alpha}(k)]b_{k\alpha}^{\dagger}|0\rangle \equiv E_{k\alpha}b_{k\alpha}^{\dagger}|0\rangle \qquad (3.30)$$

where we have also used the fact that $c_{is}^{\dagger}c_{is}|0\rangle = |0\rangle$ and $c_{ip_\alpha}^{\dagger}c_{ip_\beta}|0\rangle = 0$ for all sites (recall that we have neglected the double-excitation terms in the Hamiltonian). Thus, the one-exciton state (3.7) is again an eigenfunction of the Hamiltonian, with eigenvalue given by equation (3.8). Accounting for non-boson statistics, therefore, has no effect for states with zero or one exciton, as is obviously correct.

Non-boson statistics are, however, relevant for the many-exciton states defined by equation (3.9). Using the commutation relation (3.29) and noting the properties of the vacuum state, it is straightforward to show that the Hamiltonian (3.4) acting on a two-exciton state yields

$$H\, b_{k\alpha}^{\dagger} b_{k'\beta}^{\dagger}|0\rangle = (E_{k\alpha} + E_{k'\beta})b_{k\alpha}^{\dagger} b_{k'\beta}^{\dagger}|0\rangle - \frac{1}{N}\sum_{k''}(E_{k''\alpha}b_{k''\alpha}^{\dagger} b_{k+k'-k''\beta}^{\dagger}$$

$$+ E_{k''\beta}b_{k''\beta}^{\dagger} b_{k+k'-k''\alpha}^{\dagger})|0\rangle \qquad (3.31)$$

where $E_{k\alpha}$ is the appropriate one-exciton energy given by equation (3.8). The two-exciton state, $b_{k\alpha}^{\dagger} b_{k'\beta}^{\dagger}|0\rangle$, is clearly not an eigenstate of the Hamiltonian. We may, however, calculate the expectation value of the energy in this state, and this is found to be

$$E_{k\alpha\, k'\beta} \equiv \langle 0|b_{k'\beta}b_{k\alpha}\, H\, b_{k\alpha}^{\dagger} b_{k'\beta}^{\dagger}|0\rangle / \langle 0|b_{k'\beta}b_{k\alpha}\, b_{k\alpha}^{\dagger} b_{k'\beta}^{\dagger}|0\rangle$$

$$= (E_{k\alpha} + E_{k'\beta}) - (1/N)\frac{(1 + \delta_{\alpha\beta})}{[1 + \delta_{kk'}\delta_{\alpha\beta} - (1/N) - (1/N)\delta_{\alpha\beta}]}$$

$$\times (E_{k\alpha} + E_{k'\beta} - 2\Delta\epsilon). \qquad (3.32)$$

We see that there is a correction of order $O(1/N)$ to the boson result, $E_{k\alpha\, k'\beta} = E_{k\alpha} + E_{k'\beta}$, and that this correction is largest for states near to the band edges and of a sign such that the two-exciton band is narrowed. In other words, there is an attractive kinematic interaction for high-energy excitons, and a repulsive kinematic interaction for low-energy excitons.

The results become progressively more complicated as one considers more excitons. Let us therefore consider the special case of n excitons with the same wavevector and polarization, i.e. the n-exciton state

$$b_{k\alpha}^\dagger b_{k\alpha}^\dagger \ldots |0\rangle. \tag{3.33}$$

The behaviour of such states is likely to be relevant to the bandwidth of a many-exciton band, since some (though not all) states at the band edge are of this form. The expectation energy of the state (3.33) can be shown to be [36]

$$E_{k\alpha k\alpha\ldots} = n\left(E_{k\alpha} - \frac{n-1}{N-1}(E_{k\alpha} - \Delta\epsilon)\right). \tag{3.34}$$

The correction to the boson result is now of the order $O(n/N)$. This strongly suggests that an n-exciton band is narrowed by a factor of the order $O(n/N)$. In the limit $N \to \infty$, the narrowing is non-negligible if there is a macroscopic number of excitons.

We now comment on the implications of the above for the transition to an EI phase. As discussed in section 3.1, the transition occurs when the lower edge of the band of one-exciton states becomes degenerate with the ground state. Since the behaviour of one-exciton states is independent of the many-particle statistics assumed, the critical density at which the transition occurs is again given by equation (3.11).

The nature of the transition is, however, likely to be altered. Recall from section 3.1 that, when boson statistics are assumed, the bottom of all many-exciton bands also become simultaneously degenerate with the ground state at the transition, leading to the condensation of a macroscopic number of excitons. When the correct statistics are used, however, the many-exciton bands are narrowed, such that the lower edge of an n-exciton band is raised in energy by an amount of the order of $O(n/N)$. In the thermodynamic limit, therefore, the exciton bands shown in figure 1 are unaffected, but those bands consisting of a macroscopic number of excitons, which for clarity are not shown in figure 1, are narrowed. Thus, as the density is increased through ρ_c, one might expect instead a continuous increase in the number of excitons in the ground state, in contrast to the abrupt condensation of a macroscopic number of excitons suggested in section 3.1. That is, the presence of a kinematic interaction between excitons seems likely to drive the transition second order.

3.4. Double-excitation terms, correct statistics

So far, we have considered separately the effects of double-excitation terms and non-boson statistics on the results of the simple model studied in section 3.1. We now examine their combined effect, and thus study the full model Hamiltonian given by equation (3.1).

As in section 3.2, we remove the double-excitation terms via the transformation (3.13), and consequently we need to know the commutation properties of the operators $B_{k\alpha}$. From the definition of the operators $B_{k\alpha}$, it follows that the commutation properties may be related to those of the operators $b_{k\alpha}$ by

$$[B_{k\alpha}, B_{k'\beta}] = \cosh\theta_{k\alpha}\sinh\theta_{k'\beta}[b_{k\alpha}, b_{-k'\beta}^\dagger] - \sinh\theta_{k\alpha}\cosh\theta_{k'\beta}[b_{k'\beta}, b_{-k\alpha}^\dagger]$$
$$\tag{3.35}$$

$$[B_{k\alpha}^\dagger, B_{k'\beta}^\dagger] = \sinh\theta_{k\alpha}\cosh\theta_{k'\beta}[b_{-k\alpha}, b_{k'\beta}^\dagger] - \cosh\theta_{k\alpha}\sinh\theta_{k'\beta}[b_{-k'\beta}, b_{k\alpha}^\dagger]$$
(3.36)

$$[B_{k\alpha}, B_{k'\beta}^\dagger] = \cosh\theta_{k\alpha}\cosh\theta_{k'\beta}[b_{k\alpha}, b_{k'\beta}^\dagger] - \sinh\theta_{k\alpha}\sinh\theta_{k'\beta}[b_{-k'\beta}, b_{-k\alpha}^\dagger]$$
(3.37)

where we have used equation (3.28) to eliminate two terms in each expression. We will find the following special case of equation (3.37) useful:

$$[B_{k\alpha}, B_{k\alpha}^\dagger] = \frac{1}{N}\sum_i(c_{is}^\dagger c_{is} - c_{ip_\alpha}^\dagger c_{ip_\alpha})$$
(3.38)

where we have used equation (3.29). Note that the transformation (3.13) is not canonical when the correct statistics are taken into account.

Beginning from the Hamiltonian (3.1), and using the transformations (3.3) and (3.13), one finds the following form for the Hamiltonian:

$$H = \frac{1}{2}\sum_{k\alpha}\{[\![\{[\Delta\epsilon - \rho M^2 D^{\alpha\alpha}(k)]^2 - [\rho M^2 D^{\alpha\alpha}(k)]^2\}^{1/2} + \Delta\epsilon]\!]B_{k\alpha}^\dagger B_{k\alpha}$$
$$+ [\![\{[\Delta\epsilon - \rho M^2 D^{\alpha\alpha}(k)]^2 - [\rho M^2 D^{\alpha\alpha}(k)]^2\}^{1/2} - \Delta\epsilon]\!]B_{k\alpha}B_{k\alpha}^\dagger\}.$$
(3.39)

In deriving equation (3.39), we have used equations (3.6), (3.14), (3.16) and (3.17), but have made no assumptions about the commutation properties of the operators. If one assumes Bose–Einstein statistics, then equation (3.18) is recovered.

Consider the vacuum state defined in section 3.2, and the single- and many-renormalized-exciton states defined in equations (3.19) and (3.21). As discussed in section 3.2, the presence of the double-excitation terms means that, even for densities $\rho < \rho_c$, there is a macroscopic number of bare excitons in each of these states, including the vacuum state. Thus, in contrast to the situation described in section 3.3, the assumption of Bose–Einstein statistics does not hold in *any* of these states. In fact, neither the vacuum state, the single-renormalized-exciton states, nor the many-renormalized-exciton states are eigenstates of the Hamiltonian (3.39). As in section 3.3, we must evaluate the expectation energies of these states.

First, however, we calculate the expectation value of the number of bare excitons, or equivalently the expectation value of the number of excited sites, per site in the vacuum state, $|0\rangle$:

$$\langle n\rangle_{(0)} \equiv \frac{1}{N}\sum_{i\alpha}\langle 0|b_{i\alpha}^\dagger b_{i\alpha}|0\rangle = \frac{1}{N}\sum_{k\alpha}\langle 0|b_{k\alpha}^\dagger b_{k\alpha}|0\rangle$$
$$= \frac{1}{N}\sum_{k\alpha}\sinh^2\theta_{k\alpha}\langle 0|[B_{-k\alpha}, B_{-k\alpha}^\dagger]|0\rangle$$
(3.40)

where we have used the fact that $B_{-k\alpha}$ destroys the vacuum state to replace $B_{-k\alpha}B_{-k\alpha}^\dagger$ by the commutator. Now, from equation (3.38), the commutator is independent of k. The right-hand side of equation (3.40) thus depends on the sum

$\sum_{k} \sinh^{2} \theta_{k\alpha}$ and, since this is clearly independent of α, we may rewrite equation (3.40):

$$\langle n \rangle_{(0)} = \left(\frac{1}{N} \sum_{k} \sinh^{2} \theta_{k\alpha} \right) \sum_{\alpha} \left\langle 0 \left| \frac{1}{N} \sum_{i} (c_{is}^{\dagger} c_{is} - c_{ip_{\alpha}}^{\dagger} c_{ip_{\alpha}}) \right| 0 \right\rangle$$

$$= \left(\frac{1}{N} \sum_{k} \sinh^{2} \theta_{k\alpha} \right) \left(3 - \frac{4}{N} \sum_{i\alpha} \langle 0 | b_{i\alpha}^{\dagger} b_{i\alpha} | 0 \rangle \right). \tag{3.41}$$

Finally, rearranging we find

$$\langle n \rangle_{(0)} = \frac{(1/N) \sum_{k\alpha} \sinh^{2} \theta_{k\alpha}}{1 + (4/3N) \sum_{k\alpha} \sinh^{2} \theta_{k\alpha}} = \frac{\langle n \rangle_{(0)}^{bos}}{1 + \frac{4}{3} \langle n \rangle_{(0)}^{bos}} \tag{3.42}$$

where $\langle n \rangle_{(0)}^{bos}$ is given by equation (3.23).

We see that $\langle n \rangle_{(0)}$ lies in the range $0 \leqslant \langle n \rangle_{(0)} \leqslant 3/4$, the upper limit occurring when the s orbital and the three p orbitals of each site contribute equally to the vacuum state. This is in contrast to the corresponding result in the boson approximation, for which $\langle n \rangle_{(0)}^{bos}$, given by equation (3.23), is not in principle bounded above. The former result is clearly the physically correct one. More generally, the effect of including the correct many-particle statistics is always to lower somewhat the expectation value of the number of excited sites in the vacuum state. For an FCC lattice at the transition density, for example, $\langle n \rangle_{(0)} = 0.077$, in contrast to the result given in section 3.2, $\langle n \rangle_{(0)}^{bos} = 0.086$.

Using the fact that $B_{k\alpha}$ destroys the ground state, the ground state energy per site is given by

$$E_{(0)} = \frac{1}{2N} \sum_{k\alpha} [\{ [\Delta \epsilon - \rho M^{2} D^{\alpha\alpha}(k)]^{2} - [\rho M^{2} D^{\alpha\alpha}(k)]^{2} \}^{1/2} - \Delta \epsilon]$$

$$\times \langle 0 | [B_{k\alpha}, B_{k\alpha}^{\dagger}] | 0 \rangle \tag{3.43}$$

and using equation (3.38) this reduces to

$$E_{(0)} = E_{(0)}^{bos} (1 - \tfrac{4}{3} \langle n \rangle_{(0)}) \tag{3.44}$$

where $E_{(0)}^{bos}$ is given by equation (3.24) and $\langle n \rangle_{(0)}$ by equation (3.42). Remembering that $E_{(0)}^{bos}$ is negative, we see that the energy of the ground state is greater than the boson result by a factor related to the expectation value of the number of excited sites in the ground state.

We have not been able to find a simple form for the expectation energies of the excited states. However, it would seem reasonable to suppose that an excited state, ν, is raised in energy by an amount related to the expectation value of the number of excited sites in that state, $\langle n \rangle_{(\nu)}$. By analogy with the findings of section 3.3, we may also suppose that bands of many renormalized excitons, as well as being increased in energy as a whole, are narrowed. The critical density for a transition to an EI

phase is determined by the energy gap between the ground state and the bottom of the first excited band. The correction to the boson result (equation (3.25)) is thus expected to be of the order of the difference between $\langle n \rangle_{(0)}$ and $\langle n \rangle_{(1)}$, which we may suppose to be small at all densities. If this is true, then the critical density is again given by equation (3.25). If, as we have suggested, higher many-renormalized-exciton bands are both increased in energy and narrowed, relative to lower bands, then the transition is likely to be driven second order, as suggested in section 3.3.

We thus arrive at the following picture for the transition to a Frenkel EI phase of the model system. For densities $\rho < \rho_c$, the ground state of the system is the vacuum state defined in section 3.2. This state is non-dipolar but does contain a non-zero fraction of excited sites (of the order of 10% at $\rho = \rho_c$). At the density $\rho = \rho_c$ given by equation (3.25), which is half that predicted in the absence of double-excitation terms, each site acquires a non-zero dipole moment, and there is a transition to a dipolar Frenkel EI phase. Incorporation of non-boson statistics is expected to drive the transition second order, so that the site dipole moment increases continuously from zero at the transition. The expectation value of the number of excited sites in the ground state is also likely to increase sharply but continuously at the transition. Hence, it is the site dipole moment, and not the expectation value of the number of excited sites in the ground state, that is the appropriate order parameter for the transition. The procedures described so far, however, cannot address explicitly the evolution of this order parameter through the transition.

4. Hartree approximation

We now turn to the Hartree approximation to the model Hamiltonian, given by equation (2.10), which, as we shall see, also predicts a transition to a Frenkel EI phase as the density of the system is increased. Within the Hartree approximation, one can address the approach to the transition and predict the critical density at which the transition occurs, and these results will be compared with the predictions of the pairing theory. Furthermore, and in contrast to the pairing theory, one can also describe the dipolar phase, and thus describe the evolution of the order parameter, the site dipole moment, through the transition. To facilitate comparison with the results of the pairing theory, we again consider the simple example introduced in the previous section: an infinite Bravais lattice with $\Delta \epsilon_i = \Delta \epsilon$ for all i.

It is first convenient to recast the Hamiltonian (2.10) in terms of the expectation value of the site dipole moment, whence the problem takes the form of a self-consistent calculation of the dipole moment. For the system of neutral one-electron sites that we are considering, the operator for the dipole moment on site i is given by

$$\hat{\mu}_i = -\sum_{\alpha} M_{\alpha} (c_{is}^{\dagger} c_{ip_{\alpha}} + c_{ip_{\alpha}}^{\dagger} c_{is}) \tag{4.1}$$

where

$$M_{\alpha} = \langle is | e(r - R_i) | ip_{\alpha} \rangle \tag{4.2}$$

is a vector (assumed real) whose only non-zero component is the α component, which takes the value M. Thus, the expectation value of the dipole moment on site i is

given by

$$\mu_i = -\sum_\alpha M_\alpha (\langle c_{is}^\dagger c_{ip_\alpha} \rangle + \langle c_{ip_\alpha}^\dagger c_{is} \rangle) \tag{4.3}$$

where $\langle \ldots \rangle$ denotes an expectation value in the state of interest. Using equation (4.3), the Hamiltonian (2.10) may be rewritten in the physically appealing form

$$H = \sum_i \left(\sum_\alpha \Delta\epsilon\, c_{ip_\alpha}^\dagger c_{ip_\alpha} + \sum_\alpha M_\alpha \cdot E_i (c_{is}^\dagger c_{ip_\alpha} + c_{ip_\alpha}^\dagger c_{is}) \right) + \frac{1}{2} \sum_{i \neq j} \mu_i T_{ij} \mu_j \tag{4.4}$$

where

$$\mathbf{T}_{ij} = \left(\frac{3(R_j - R_i)(R_j - R_i)}{|R_j - R_i|^5} - \frac{1}{|R_j - R_i|^3} \right) \tag{4.5}$$

is the dipole–dipole interaction tensor and

$$E_i = \sum_{j(\neq i)} \mathbf{T}_{ij} \cdot \mu_j. \tag{4.6}$$

The right-hand side of equation (4.4) consists of a sum of N atomic Hamiltonians, plus a classical term that contributes to the total energy, but not to the quantum mechanics, of the system. Each atomic Hamiltonian is of a form corresponding to an isolated four-level atom in an electric field, E_i. The atoms are not, of course, independent, since the electric field, E_i, experienced by an atom i arises from dipolar fields due to putative dipoles on all atoms $j \neq i$ (see equation (4.6)), and thus depends on the expectation value of the dipole moment on all other atoms. The diagonalization of Hamiltonian (4.4) is, in fact, a matter of self-consistency since the expectation value of the dipole on any atom both helps to determine and is determined by the dipoles on all other atoms.

One sees from equation (4.6) that, because $\mathbf{T}_{ij}$ is not diagonal, a dipole moment in, say, the z direction may contribute to the x component of the electric field felt at site i. In other words, the different polarizations of the atomic dipoles are, in general, closely intertwined. The problem is simplified if we neglect the effects of the off-diagonal elements of $\mathbf{T}_{ij}$. In fact, this approximation is directly equivalent to that used in the pairing theory, of neglecting the cross-terms in the second term on the right-hand side of equation (2.7). As discussed in sections 2 and 3.1, this does not affect the transition to an EI phase in primitive cubic lattices. It would therefore seem a reasonable approximation to neglect the off-diagonal elements of $\mathbf{T}_{ij}$, and we do so here.

Solution of the problem posed by Hamiltonian (4.4) amounts to a self-consistent determination of the expectation dipole moments of all N sites. If there exists more than one self-consistent solution, then the ground-state configuration of dipole moments corresponds to that with the lowest energy. One configuration that is always possible is, of course, that with zero dipole moment on all sites, but this is not necessarily the lowest-energy solution, as we show below.

The simplest way to proceed is to allow for the possibility of a ferroelectric state, *with the dipole moment of equal magnitude and orientation on all sites*. Diagonalization of Hamiltonian (4.4) then leads to a self-consistency equation to be solved for the magnitude of the dipole moment. We can, however, be somewhat more general than this. Since we neglect the effects of the off-diagonal elements of T_{ij}, we may consider the three components of the dipole moment separately. Suppose that the α component of the dipole moment is of equal magnitude on all sites, but may, for any site, be orientated in a positive or negative direction. We thus allow in addition for the further possibility of antiferroelectric configurations of dipole moments. Then, the α component of the dipole moment on site j may be written

$$\mu_j^{(\alpha)} = \mu_\alpha e^{ik_\alpha \cdot R_j} \qquad (4.7)$$

where μ_α is the magnitude, common to all sites, and k_α is the wavevector associated with a set of orientations. k_α is restricted to those values such that $e^{ik_\alpha \cdot R_j} = \pm 1$ for all sites j. The α component of the field felt at site i is then given, using equation (4.6), by

$$E_i^{(\alpha)} = \mu_\alpha \sum_{j(\neq i)} T_{ij}^{\alpha\alpha} e^{ik_\alpha \cdot R_j} = \rho \mu_\alpha e^{ik_\alpha \cdot R_i} D^{\alpha\alpha}(k_\alpha) \qquad (4.8)$$

where $D^{\alpha\alpha}(k_\alpha)$ is defined by equation (3.5). Equation (4.8) is the form of the electric field that we use in the Hamiltonian (4.4).

Equation (4.7), with $\alpha = x, y, z$, describes the assumed configuration of dipole moments. The range of possible values of k_α allows for a range of possible configurations, e.g. a ferroelectric configuration is obtained by setting $k_\alpha = (0,0,0)$, whereas $k_\alpha = (0,0,\pi/a)$ (a is an appropriate lattice constant) represents a configuration that is antiferroelectric parallel to the z axis. For an arbitrary choice of k_α, a self-consistent solution yields possible values for the magnitudes, μ_α. The self-consistent solution proceeds as follows.

Having assumed a configuration of dipoles, of the form given by equation (4.7), we diagonalize the Hamiltonian for a site i. The resulting expectation value of the dipole moment of site i must be consistent with the assumed configuration of dipoles. It is simplest to assume that only one p orbital, say the p_z orbital, contributes to the dipole moment of a site. This involves no loss of generality, since we have made no assumptions about the direction of spatial quantization of the p orbitals: all information about the orientation of the p orbitals relative to the crystal axes is contained in the dipole sum, $D^{\alpha\alpha}(k_\alpha)$. The trial Hartree wavefunction is then a suitably antisymmetrized product of N atomic wavefunctions of the form

$$a_{is}|is\rangle + a_{ip_z}|ip_z\rangle \qquad (4.9)$$

where a_{is} and a_{ip_z} are coefficients (assumed real) to be determined, and the relevant part of the Hamiltonian for site i reduces to

$$H_i = \Delta\epsilon\, c_{ip_z}^\dagger c_{ip_z} + M E_i^{(z)}(c_{is}^\dagger c_{ip_z} + c_{ip_z}^\dagger c_{is}). \qquad (4.10)$$

Solving this simple eigenvalue problem, we find that the lowest-energy state has a dipole moment given by

$$\left(\mu_i^{(z)}\right)^2 = \mu_z^2 = \frac{4\rho^2 M^4 [D^{zz}(k_z)]^2 \mu_z^2}{\Delta\epsilon^2 + 4\rho^2 M^2 [D^{zz}(k_z)]^2 \mu_z^2}. \qquad (4.11)$$

and energy

$$E = \tfrac{1}{2}\Delta\epsilon - \tfrac{1}{2}\{\Delta\epsilon^2 + 4\rho^2 M^2 [D^{zz}(k_z)]^2 \mu_z^2\}^{1/2} \tag{4.12}$$

where we have used the fact that $(e^{ik_a \cdot R_i})^2 = 1$. The self-consistency of the problem is evident from equation (4.11), where we have assumed the derived dipole moment of site i to be of the form assumed initially, i.e. of the form given in equation (4.7). Adding in the last (classical) term of equation (4.4), the total energy per site is

$$E = \tfrac{1}{2}\Delta\epsilon - \tfrac{1}{2}\{\Delta\epsilon^2 + 4\rho^2 M^2 [D^{zz}(k_z)]^2 \mu_z^2\}^{1/2} + \tfrac{1}{2}\rho D^{zz}(k_z)\mu_z^2. \tag{4.13}$$

Equations (4.11) and (4.13) always possess a solution

$$\mu_z = 0 \qquad E = 0 \tag{4.14}$$

i.e. the zero-energy non-dipolar state with all electrons in s orbitals. However, for densities larger than a critical density

$$\rho_c = \frac{\Delta\epsilon}{2M^2 D^{zz}(k_z)} \tag{4.15}$$

there is also a solution corresponding to a dipolar state with dipole moment

$$\mu_z^2 = M^2 - \frac{\Delta\epsilon^2}{4\rho^2 M^2 [D^{zz}(k_z)]^2} \tag{4.16}$$

and energy

$$E = \tfrac{1}{2}\Delta\epsilon - \tfrac{1}{2}\rho M^2 D^{zz}(k_z) - \tfrac{1}{8}[\Delta\epsilon^2/\rho M^2 D^{zz}(k_z)]. \tag{4.17}$$

When this solution exists, i.e. for densities $\rho > \rho_c$, we see from equation (4.17) that the energy of the dipolar state is negative. Thus, the dipolar state, when possible, is energetically stable with respect to the zero-energy non-dipolar state.

We see from equation (4.15), that the critical density at which the dipolar state appears depends on the configuration of putative dipoles, characterized by the value of k_z, that we have assumed. To predict a value for ρ_c, we clearly need to specify k_z. The particular dipolar state—ferroelectric or antiferroelectric—which is in fact realized is that characterized by a wavevector k_z such that the energy (given by equation (4.17)) is minimized. It is, therefore, this wavevector that enters equation (4.15) when predicting the critical density for the transition to the EI phase.

We now summarize as follows: For densities lower than ρ_c (as given by equation (4.15)), the ground state is non-dipolar with a constant energy of zero. As ρ increases through ρ_c, each atom develops a non-zero dipole moment:

$$\mu_z^2 = M^2 \left(1 - \frac{\rho_c^2}{\rho^2}\right) \qquad \rho > \rho_c \tag{4.18}$$

Initially, the dipole increases as a function of density with a mean-field exponent of $1/2$. For higher densities, however, the dipole moment magnitude asymptotically

approaches its limiting value of M, owing to the finite basis set that we have assumed. The energy per site of the dipolar state is

$$E = \frac{1}{2}\Delta\epsilon\left(1 - \frac{1}{2}\frac{\rho_c}{\rho} - \frac{1}{2}\frac{\rho}{\rho_c}\right) \qquad \rho > \rho_c. \tag{4.19}$$

The wavevector that minimizes the energy of the dipolar state, and thus enters equation (4.15), is that for which $D^{zz}(k_z)$ is a maximum. This wavevector is thus also that associated with the bottom of the band of renormalized excitons. Hence, the critical density predicted by equation (4.15) is precisely that predicted by the pairing theory (see equation (3.25)). Further, the second-order nature of the transition suggested by the pairing theory (see section 3.4) also results from the Hartree approach. Therefore, for the system under study, the Hartree approximation appears to describe the transition well. Further, equation (4.14) for $\rho < \rho_c$ and equation (4.18) for $\rho > \rho_c$ give an explicit form for the evolution of the order parameter (which, as we argued in section 3, is the magnitude of the site dipole moment) through the transition. One feature, however, that the Hartree approximation fails to reproduce is the van der Waals binding energy: for densities less than the critical density, the ground-state energy is independent of density. A corollary to this is that, in contrast to the results of the pairing theory, the Hartree approximation predicts a zero density of excited sites for $\rho < \rho_c$. These discrepancies, however, are not relevant to the question of the existence of an EI phase.

Finally, we consider how the above results are altered if one neglects the double-excitation terms in the model Hartree Hamiltonian. Assuming $\langle c^\dagger_{is}c_{ip_\alpha}\rangle$ to be real, this results simply in factors of $1/2$ appearing in the terms in the second and third lines of equation (2.10). Solving the resultant Hamiltonian as before, we recover the results of equations (4.14)–(4.19) except that factors of $D^{zz}(k_z)$ are replaced by factors of $(1/2)D^{zz}(k_z)$. In particular, equations (4.14), (4.18) and (4.19) are retained unchanged, but the critical density is twice the value given in equation (4.15). This doubling of the critical density is in agreement with the results of section 3.

5. Discussion

In section 3, we studied the model system via the pairing theory, making solely the assumption that terms connecting different polarizations could be neglected, an assumption we argued was justified for a study of the transition to an EI phase. In the event, a full study of the effects of non-boson statistics was not found to be possible, but we feel that sufficient is known for one to be reasonably confident about the occurrence and nature of the transition to the EI phase. At a certain critical density, for which an expression was given, the model system is predicted to undergo a second-order transition to an EI phase. The importance of the double-excitation terms on the critical density was emphasized.

The method for dealing with the double-excitation terms (the Bogoliubov transformation) is specific to systems with translational symmetry. Frenkel EI phases, however, have been postulated for some systems that lack translational symmetry, e.g. expanded fluid mercury [7–10], and alkali metals in ammonia [14–16] and alkali-metal halide [17, 18] solutions. A more general, albeit approximate, approach is

provided by the Hartree decoupling scheme. The Hartree approximation is applicable to disordered, as well as crystalline, systems, and has the added advantage that it provides a description of the dipolar state. As mentioned in section 2, however, there is no *a priori* way of knowing how good the Hartree approximation is, and so in section 4 we compared the results with those of the pairing theory for the lattice system under study. Excellent agreement was found: the expression for the critical density, both with and without the presence of the double-excitation terms, was recovered, as well as the fact that the transition is second order. Thus, the Hartree approximation is certainly adequate for lattice systems, and it seems reasonable to suppose that it may also be used for systems that the pairing approach cannot easily deal with, i.e. disordered systems.

We see, therefore, that the model Hamiltonian has a stable EI phase at high enough densities. Whether real systems exhibit such a Frenkel EI phase depends on whether the model Hamiltonian (applicable at low densities) is still valid at the critical density of the transition. One possible correction to the model Hamiltonian, which has already been mentioned, is to replace the matrix elements (2.2) by a more general form, taken, for example, from detailed spectroscopic calculations [10]. Although this will change the numerical value of the critical density, it will not change any of the qualitative conclusions; in particular, the model system will still have a stable EI phase. Alternatively, one may include the two classes of term described after equation (2.4), which were neglected in constructing Hamiltonian (2.1). One possible effect of these is to lead to the formation of polyexcitons [29–31] (although such effects are expected to be more important for polar molecules [30, 31]) and, as yet, the consequences of this for the putative EI phase are not known. The most important correction, however, is to include one-electron hopping matrix elements. If a real system does possess a transition to a Frenkel EI phase then, as the density is increased further, the one-electron hopping elements will cause the Frenkel EI state to evolve into a Mott–Wannier EI state, followed by a metallic phase via a Mott unbinding transition [42]. In many systems, however, the effects of the one-electron hopping elements will be so dominant that there is a transition directly from the non-dipolar insulator to a metallic phase, with no intervening EI phase.

We should also point out that we have assumed a zero-temperature formalism, so that the number density of sites is the only thermodynamic variable. Within this picture, the EI phase of a lattice-based system possesses a regular array of dipoles, characterized by some wavevector. The situation is modified at non-zero temperatures. As the temperature is increased, for a given density above the critical density, the correlation between dipoles on different sites decreases until, at a high enough temperature, the long-range ordering of dipoles vanishes, i.e. there is a transition to a paraelectric phase. Alternatively, for a constant but high temperature, one expects a transition at a density $\rho_c(T)$ to a dipolar state that is paraelectric rather than ferroelectric [10].

To get an idea of the thermal energies required to destroy the long-range ordering of dipoles inherent in the results of section 4, consider the energy needed to invert a dipole on a single site, i, namely

$$2 \sum_{j(\neq i)} \mu_i T_{ij} \mu_j. \qquad (5.1)$$

Assuming that all dipoles are aligned parallel or antiparallel to the z axis, and using

equation (4.7), expression (5.1) may be written as

$$2\rho\mu_z^2 D^{zz}(k_z).$$

(5.2)

Finally, substituting for μ_z from equation (4.18) and for $D^{zz}(k_z)$ from equation (4.15), the energy required takes the form

$$\Delta\epsilon \frac{\rho}{\rho_c}\left(1 - \frac{\rho_c^2}{\rho^2}\right).$$

(5.3)

When $\rho/\rho_c = 1.3$, this energy is half the zero-density excitation energy, $\Delta\epsilon$, and consequently may be of the order of an eV. Thus, as one passes into the EI phase, there is only a relatively narrow range of density before extremely high temperatures are needed to destroy the dipole ordering.

We have also assumed in this paper that the site density, ρ, is a thermodynamic variable that we may choose at will, i.e. that does not depend on the electronic structure that we are investigating. The significant changes in the electronic structure that accompany the transition to an EI phase, however, may have an effect on the structure that the ions adopt [24, 25]. More specifically, one consequence of the transition to an EI phase may be that the system is thermodynamically unstable for a range of densities encompassing the critical density of the transition, ρ_c. If this is the case, then, as the density is increased, the system will jump discontinuously from some density below the calculated second-order transition to another density above it. Thus, the observed transition will be first order, and accompanied by a discontinuous volume change [43].

The above discussion is appropriate to an infinite system. We conclude by presenting a simple example of a finite system: a two-site system in which each site is associated with one s orbital and three p orbitals. The two sites are labelled 1 and 2, and are separated by a distance R. We assume the internuclear axis to lie parallel to the z axis. The model Hamiltonian, equation (2.5), then reduces to

$$H = \sum_\alpha [\Delta\epsilon\, c_{1p_\alpha}^\dagger c_{1p_\alpha} + \Delta\epsilon\, c_{2p_\alpha}^\dagger c_{2p_\alpha} - P_{12}^{sp_\alpha,sp_\alpha}(c_{1s}^\dagger c_{1p_\alpha} + c_{1p_\alpha}^\dagger c_{1s})(c_{2s}^\dagger c_{2p_\alpha} + c_{2p_\alpha}^\dagger c_{2s})]$$

(5.4)

where we have defined the zero of energy such that $\epsilon_{1s} + \epsilon_{2s} = 0$, and we have assumed $\Delta\epsilon_i = \Delta\epsilon$ for $i = 1, 2$. For this system, the cross-terms in $P_{12}^{sp_\alpha,sp_\beta}$ ($\alpha \neq \beta$) are all zero.

This simple two-site problem may be solved within the Hartree approximation in precisely the way described in section 4. One then arrives at the following solution. For internuclear separations greater than a critical separation, R_c, the ground state is non-dipolar with a constant energy of zero. As the internuclear separation decreases through R_c, however, both sites develop a non-zero dipole moment, with both dipoles aligned along the internuclear axis and orientated in the same direction. The critical separation is given by

$$R_c = \left(\frac{4M^2}{\Delta\epsilon}\right)^{1/3}$$

(5.5)

An exact solution for Hamiltonian (5.4) yields a different picture. For this simple example, there are 16 possible electron configurations, allowing for each electron to be in one of four possible orbitals. Diagonalising Hamiltonian (5.4), we therefore have 16 exact eigenstates of the system. The ground state is a mixture of the configuration with both electrons in s orbitals and the three configurations with both electrons in p_α orbitals ($\alpha = x, y, z$), and has an energy $\Delta\epsilon - (\Delta\epsilon^2 + 6M^4/R^6)^{1/2}$. The lowest excited state is a mixture of the configuration with the electron on site 1 in an s orbital and the electron on site 2 in a p_z orbital, and the configuration with the electron on site 1 in a p_z orbital and the electron on site 2 in an s orbital, and has an energy of $\Delta\epsilon - 2M^2/R^3$. In the language of section 2, the ground state contains only configurations with even numbers of excited sites, and thus possesses no dipole moment. There is clearly always a finite energy gap between the ground state and the lowest excited state, which contain a single excitation, and thus a finite electric field is required to produce a dipolar state.

Hence, with no external electric field present, the Hamiltonian (5.4) does not possess a dipolar ground state, and the results of the Hartree approximation are clearly incorrect. Similar conclusions follow from an analysis of a linear three-site system with an sp^3 basis. Inherent in the Hartree Hamiltonian is the possibility of a term that connects configurations with even numbers of excited sites to configurations with odd numbers of excited sites, thus producing a dipolar state (i.e. the term in the effective electric field, E_i). This term is absent in the exact Hamiltonian. In an infinite system, this term mimics well the behaviour of the exact Hamiltonian, but, as we have just seen, it leads to erroneous results in small finite systems. How one interpolates correctly between the behaviour of macroscopic systems and that of small clusters is still an open problem.

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