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# The dipolar Frenkel excitonic insulator phase of an impurity in a liquid solvent: theory

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**Abstract.** A theory of the dipolar Frenkel excitonic insulator (EI) phase developed in an earlier paper is extended to spatially disordered systems. Using the Hartree approximation studied previously, we derive, for a given atomic centre-of-mass configuration, a self-consistency equation for the atomic dipole moments, a non-zero solution to which indicates an EI phase. We obtain as a special case the microscopic Yvon–Kirkwood equations of classical dielectric theory. For the experimentally relevant case of an impurity at infinite dilution in a solvent or disordered matrix, we derive an explicit expression for the impurity dipole moment. To take into account the ensemble of atomic configurations a mean field approximation is developed, numerical results for which, within the class of linear approximations of classical liquid state theory, will be given in a subsequent paper. We also examine the dynamic response of the impurity system to an oscillating electric field. We locate the lowest excited state of the system in both the normal insulating and dipolar EI phases, and show that it is degenerate with the ground state at the EI transition, thus making contact with exciton theories of the EI phase.

## 1. Introduction

Over the past decade, there has been much interest in the possibility of observing an excitonic insulator (EI) phase arising from the condensation of Frenkel excitons. This interest has been motivated by a number of unusual experimental results [1–5], which may indicate the formation of a Frenkel EI phase. Furthermore, computer simulations of experimentally important systems [6, 7] have yielded examples of a dipolar atomic state, characteristic of the Frenkel EI phase. A summary of these results, together with an account of the theories put forward to date for describing the Frenkel EI phase [2, 8–18], can be found in our earlier paper [19] (hereafter referred to as I).

Theories of the dipolar Frenkel EI phase can be classified broadly into two approaches. The first [8–11, 13, 18] is similar in spirit to the earlier theories of the Mott–Wannier EI phase [20–25]. A transition from the normal insulating phase to an EI phase is deemed to occur when excited states of the system mix into the ground state, which in turn occurs when the ground and lowest excited states become degenerate. For a Frenkel EI phase, the relevant excited states are the band of Frenkel excitons, and the transition occurs when the lower edge of this band becomes degenerate with the ground state. In the second approach [2, 12, 14–17], the dipolar nature of the constituent atoms in the Frenkel EI phase is emphasized. The central question is whether or not the interaction between the putative dipole moment of an atom and its polarized surroundings is sufficient to stabilize the formation of an atomic dipole, and thus yield a Frenkel EI phase.

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In I, we gave a critical discussion of two alternative analyses of a model system, which exemplify the two general approaches to the Frenkel EI phase described above. The first analysis, which we termed 'pairing theory', yields the Frenkel exciton band of the model system, the broadening of which can be followed as a function of system density, and the transition to the EI phase predicted as described above. We showed in I that to get a reliable estimate of the transition density, one must include the so-called 'double excitation' terms in the model Hamiltonian. With this, solution of the resulting problem is straightforward for a crystalline system, but difficult for any spatially disordered system.

The majority of candidates for the realization of a Frenkel EI phase are, however, spatially disordered systems—liquids or amorphous solids [1–3, 5–7]—since in these the excitons are commonly tightly bound, and thus of Frenkel type. In crystalline systems, the excitons are more usually of Mott–Wannier type. The pairing theory, though allowing a rigorous analysis, is therefore of limited usefulness, since it cannot deal reliably with the disordered systems which are of primary interest. Furthermore, although one can use the pairing theory to locate the transition to the Frenkel EI phase, it cannot be used to describe the EI phase itself.

The second analysis examined in I is based on a Hartree decoupling of the electron correlation terms that give rise to the exciton states. For the assumed basis, diagonalization of the Hartree Hamiltonian yields the dipole moment of an atom in terms of the local electric field arising from the dipole moments of all other atoms. Evaluation of the dipole moments is thus a matter of self-consistency, and only for a high enough system density is there a solution possessing non-zero dipole moments. The Hartree approximation yields both the transition density, and the atomic dipole moment in the Frenkel EI phase.

In I, we found excellent agreement between the results of the Hartree approximation and those of the pairing theory, for a crystalline model system. The Hartree approximation thus appears to form a reliable approach. It has the two advantages that it allows a description of the Frenkel EI phase itself, and is applicable to non-crystalline systems. The purpose of the present paper is to extend the results of I for the Hartree approximation to spatially disordered systems. For a particular configuration of atoms, the formal application of the theory of I is straightforward. For a spatially disordered system, however, one must take account of the ensemble of possible centre-of-mass configurations, and this consideration forms much of the present paper.

We are also able to throw more light on the connection between the Hartree approach and the pairing theory, by an investigation of the excited states of the Hartree Hamiltonian. A study of the linear response of the system to an externally applied oscillating electric field allows one to locate the excited states, and these may be identified as exciton states analogous to those of pairing theory. It follows that the dipolar solutions to the Hartree Hamiltonian, when allowed, arise out of an admixture into the ground state of these exciton states.

As mentioned above, the Hartree approximation yields the dipole moment of an atom in terms of the local electric field arising from the dipole moments of all other atoms. The response of each atom to the local field is found to be non-linear, an essential feature for the formation of an EI phase. Local electric fields in condensed phases can indeed be very large [26], and a non-linear response to them is not unlikely. The dipolar Frenkel EI phase we wish to describe here is a dramatic consequence of this non-linearity.

From a technical point of view, however, analysis of this non-linear response is very difficult for the model system when taken in its most general form. We therefore specialize to a simplified (and relevant) case: an impurity at infinite dilution in a solvent or disordered matrix. We suppose that the non-linear response is only significant for the impurity, and

all solvent atoms are assumed to respond linearly to the local field. The possibility of a Frenkel EI phase occurring in impurity systems has been suggested by results from a number of experiments and computer simulations [2, 3, 5-7].

With this assumption, a Frenkel EI phase is still possible, and again constitutes a new (dipolar) ground state in which excited states of the system are mixed into the normal ground state. For an impurity system, however, the greatest admixture of the excited state occurs on the impurity site itself. Qualitatively, one may consider the transition to an EI phase as a change in the ground state of the impurity atom mediated by the solvent, which itself remains largely unaffected. Thus, the Frenkel EI phase for the impurity system consists of a dipolar impurity atom stabilized by interactions with the solvent.

The outline of the paper is as follows. In section 2.1, we review the model system introduced in I, and derive the self-consistency relation for the dipole moments of all atoms, which arises from the Hartree Hamiltonian. In section 2.2, we specialize to the impurity system, and give an explicit expression for the dipole moment of the impurity atom for one atomic configuration. We then discuss the question of averaging over the ensemble of atomic configurations. A suitable mean field approximation is developed, the central quantity in which is the average reaction field factor, which relates the local field at the impurity atom to the putative impurity dipole moment. In section 2.3, we describe the calculation of the average reaction field factor within the class of linear approximations of classical liquid state theory.

In section 3, we examine the linear response of the system to an externally applied oscillating electric field. From a study of the dynamic polarizability of the impurity atom, we locate the lowest excited state of the system in both the normal insulating and Frenkel EI phases. We show that this state is degenerate with the ground state at the transition, thus making contact with exciton-based theories of the EI transition. Finally, in section 4 we summarize the results, and discuss their wider implications.

## 2. Solution of Hartree equations

### 2.1. Background theory

The model system of I, which we consider again here, is based on a stationary configuration of  $N$  atoms (or 'sites'), with one valence electron per atom. The sole difference is that, in contrast to the lattice-based examples of I, we are here interested primarily in spatially disordered systems. The valence electrons are described via a tight-binding representation, and we choose a restricted basis set consisting of one s-orbital and three degenerate p-orbitals (spatially quantized along a common set of axes) per site. We assume all basis states to be mutually orthogonal.

For a given configuration of site centre-of-mass positions, the model Hamiltonian was presented as (2.5) of I. Performing a Hartree decoupling on the terms quartic in the electronic operators, and recasting the Hamiltonian in terms of the quantum mechanical expectation value of the site dipole moments  $\{\mu_j\}$ , it was shown in I that the Hamiltonian takes the following physically appealing form:

$$H = \sum_i \left( \sum_{\alpha} \Delta \epsilon_i c_{i p_{\alpha}}^{\dagger} c_{i p_{\alpha}} + \sum_{\alpha} M_{i \alpha} \cdot E_i (c_{i s}^{\dagger} c_{i p_{\alpha}} + c_{i p_{\alpha}}^{\dagger} c_{i s}) \right) + \frac{1}{2} \sum_{i \neq j} \mu_i \cdot T_{ij} \cdot \mu_j \quad (2.1)$$

This Hamiltonian forms the starting point for the analysis of the present paper.

In (2.1), the operator  $c_{is}^\dagger$  ( $c_{is}$ ) creates (annihilates) an electron in the basis state  $|is\rangle$  associated with the s orbital on site  $i$ , the operator  $c_{ip_\alpha}^\dagger$  ( $c_{ip_\alpha}$ ) creates (annihilates) an electron in the basis state  $|ip_\alpha\rangle$  associated with the  $\alpha$ -polarized p orbital on site  $i$ , and the sums run over all  $N$  sites and all three polarizations. The zero-order excitation energy is given by  $\Delta\epsilon_i = \epsilon_{ip} - \epsilon_{is}$ , where  $\epsilon_{is}$  and  $\epsilon_{ip}$  are the zero-order site energies of the s and p-levels of site  $i$ . The transition dipole moment, defined by

$$M_{i\alpha} = \langle is|e(\mathbf{r} - \mathbf{R}_i)|ip_\alpha\rangle \quad (2.2)$$

is a vector (assumed to be real) whose only non-zero component is the  $\alpha$  component, which takes the value  $M_i$ , and the dipole-dipole interaction tensor is given by

$$\mathbf{T}_{ij} = \left( \frac{3(\mathbf{R}_j - \mathbf{R}_i)(\mathbf{R}_j - \mathbf{R}_i)}{|\mathbf{R}_j - \mathbf{R}_i|^5} - \frac{\mathbf{1}}{|\mathbf{R}_j - \mathbf{R}_i|^3} \right). \quad (2.3)$$

In (2.2) and (2.3),  $-e(\mathbf{r} - \mathbf{R}_i)$  is the dipole moment operator for an electron of charge  $-e$  at position  $\mathbf{r}$ ,  $\mathbf{R}_i$  is the centre-of-mass position of site  $i$ , and  $\mathbf{1}$  is the identity matrix. The local field at site  $i$ ,  $\mathbf{E}_i$ , has been generalized to include a uniform external field,  $\mathbf{E}^{\text{ext}}$ , and is given by:

$$\mathbf{E}_i = \mathbf{E}^{\text{ext}} + \sum_{j(\neq i)} \mathbf{T}_{ij} \cdot \boldsymbol{\mu}_j. \quad (2.4)$$

Finally, the expectation value of the dipole moment on site  $i$  is

$$\boldsymbol{\mu}_i = - \sum_{\alpha} M_{i\alpha} (\langle c_{is}^\dagger c_{ip_\alpha} \rangle + \langle c_{ip_\alpha}^\dagger c_{is} \rangle) \quad (2.5)$$

where  $\langle \dots \rangle$  denotes a quantum average over the trial electronic states of the model system.

Although the model has been developed for a monovalent species, we mention that the Hamiltonian (2.1) may also be used to describe approximately a divalent species, with two valence electrons per atom. Assuming that no more than one electron is excited above the s level (which is different but consistent with the restricted basis we have used), and that the electrons are antiparallel, a simple reinterpretation of  $\Delta\epsilon_i$  in (2.1) is sufficient to model the divalent species.

The right-hand side of (2.1) consists formally 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,  $\mathbf{E}_i$ . The atoms are not, of course, independent, since the electric field,  $\mathbf{E}_i$ , experienced by an atom  $i$  arises from dipolar fields due to putative dipoles on all atoms  $j \neq i$  (see (2.4)), and thus depends on the expectation value of the dipole moment on all other atoms. The diagonalization of Hamiltonian (2.1) 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.

The solution of this problem 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 trial Hartree wavefunction is an antisymmetrized product of  $N$  atomic wavefunctions of the form

$$a_{is}|is\rangle + \sum_{\alpha} a_{ip_\alpha}|ip_\alpha\rangle. \quad (2.6)$$

Diagonalization of the atomic Hamiltonian for site  $i$  yields the eigenenergies and the corresponding eigenvector coefficients,  $a_{is}$  and  $a_{i\beta\alpha}$ , as functions of  $E_i$ . The lowest-energy solution has an eigenenergy

$$W_i = \frac{1}{2} \Delta \epsilon_i [1 - (1 + \alpha_{i0}^2 |E_i|^2 / M_i^2)^{1/2}] \quad (2.7)$$

and, assuming the average in (2.5) to be dominated by the lowest-energy state, the eigenvector coefficients of this state imply

$$\mu_i = \alpha_{i0} E_i (1 + \alpha_{i0}^2 |E_i|^2 / M_i^2)^{-1/2}. \quad (2.8)$$

In (2.7) and (2.8)

$$\alpha_{i0} = 2M_i^2 / \Delta \epsilon_i \quad (2.9)$$

is the static polarizability of site  $i$  (within the chosen basis) when it is isolated from all other sites.

For the particular centre-of-mass configuration under consideration, equations (2.8) and (2.4) constitute the required self-consistency equations for the expectation dipole moments,  $\{\mu_j\}$ . For the lattice-based system of I, and for the configuration of dipole moments assumed therein, (2.8) reduces to (4.11) of I. In the present paper, however, where the interest is in spatially disordered site configurations, we can make no *a priori* assumptions about the configuration of dipole moments, and solution of the self-consistency problem is more involved.

Equation (2.8) gives the dipole moment on site  $i$  arising from the effects of the local field  $E_i$ , and the response to the field is clearly non-linear. As shall shortly become clear, this non-linearity is crucial to the realization of a Frenkel EI phase, but first we investigate what happens if we neglect the non-linearity. Suppose that the local field is sufficiently weak that we need only consider the linear response of the dipole moment to the local field. Linearizing (2.8), we find:

$$\mu_i = \alpha_{i0} E_i = \alpha_{i0} \left( E^{\text{ext}} + \sum_{j(\neq i)} \mathbf{T}_{ij} \cdot \mu_j \right) \quad (2.10)$$

Equations (2.10), with  $i = 1, 2, \dots, N$ , are nothing other than the classical microscopic Yvon-Kirkwood equations [27,28] for the dipole moments of a system of non-polar polarizable molecules in an external field. As such, they are often used as the starting point for microscopic classical dielectric theory. It is clear, however, that in the absence of an external field the only solution to the Yvon-Kirkwood equations is that with all dipole moments zero. Linearization of (2.8), therefore, excludes the possibility of a dipolar EI phase.

The Yvon-Kirkwood equations do, however, provide some information on the possible existence of an EI phase. We show in section 3 that, in the normal insulating phase, analysis of a dynamic version of the Yvon-Kirkwood equations reveals a band of excited states, which may be identified as Frenkel excitons [29]. As discussed in section 1 and in detail in I, a transition to a Frenkel EI phase occurs when the lowest-energy exciton state becomes degenerate with the ground state. One can thus predict, via the dynamic Yvon-Kirkwood equations, the transition to an EI phase, although the EI phase itself cannot be described. Such a criterion was used by Logan and Edwards [13], using the results of Chandler and co-workers [30] for the band of excited states, to make predictions about the possibility of an EI transition in expanded fluid metals.

## 2.2. Impurity systems

We thus recover the classical Yvon–Kirkwood equations as one limit of the formal solution to the problem posed by the Hartree Hamiltonian (2.1). We have seen, however, that the Yvon–Kirkwood equations (2.10) can, at most, predict the point at which the system of interest becomes unstable with respect to an EI phase. To go beyond a stability analysis, and to describe the EI phase itself, one thus needs to retain the non-linearity embodied in (2.8). To solve the full self-consistency problem, in which every site responds non-linearly to the local field produced by the remaining  $N - 1$  sites, is clearly a formidable problem for spatially disordered systems. We therefore specialize to a particular class of systems that allow a major simplification; that of an impurity  $i$  at infinite dilution in a liquid solvent or disordered matrix.

We suppose that the polarizability of the solvent atoms,  $\alpha_0$  (for convenience, we drop the site index), is sufficiently small that we can assume a linear response to the local field. We further assume that there is no external field, i.e.  $E^{\text{ext}} = 0$ , (in section 3, we will reintroduce an oscillatory external field). The dipole moment induced on each solvent atom is thus given by an expression of the form of (2.10):

$$\mu_j = \alpha_0 E_j = \alpha_0 \sum_{k(\neq j)} \mathbf{T}_{jk} \cdot \mu_k \quad j \neq i. \quad (2.11)$$

In contrast, the polarizability of the impurity atom,  $\alpha_{i0}$ , is taken to be large ( $\alpha_{i0} \gg \alpha_0$ ), and we retain (2.8) for the impurity site. In other words, only the impurity responds non-linearly to the local field. If a Frenkel EI phase is realized in this model system, then we expect the largest dipole moment to occur on the impurity site. The primary concern is therefore whether or not the solvent can stabilize a dipolar atom at the impurity site. As mentioned in section 1, this situation is pertinent to several of the experimental candidates for the Frenkel EI phase.

To make progress with (2.8) for the impurity atom, we obtain a closed expression for  $E_i$  via repeated iteration of (2.11) for the solvent dipole moments, which yields

$$E_i = \sum_j \mathbf{T}_{ij} \cdot \mu_j = \alpha_0 \sum_j \mathbf{T}_{ij} \cdot \mathbf{T}_{ji} \cdot \mu_i + \alpha_0^2 \sum_{jk} \mathbf{T}_{ij} \cdot \mathbf{T}_{jk} \cdot \mathbf{T}_{ki} \cdot \mu_i + \dots \equiv \mathcal{G} \cdot \mu_i. \quad (2.12)$$

Here

$$\mathcal{G} = \alpha_0 \sum_j \mathbf{T}_{ij} \cdot \mathbf{T}_{ji} + \alpha_0^2 \sum_{jk} \mathbf{T}_{ij} \cdot \mathbf{T}_{jk} \cdot \mathbf{T}_{ki} + \dots \quad (2.13)$$

is the sum of all contracted  $\mathbf{T}$ -tensor products which begin and end at the impurity site, but which do not have the impurity as an intermediate site. A product of  $n$   $\mathbf{T}$ -tensors is associated with  $n - 1$  factors of  $\alpha_0$ . For the given configuration of site centre-of-mass positions,  $\mathcal{G}$  may be interpreted as the reaction field factor, which relates the local field felt at the impurity site to the dipole moment at that site. Note that  $\mathcal{G}$  depends only on the dipole–dipole interaction tensor and the solvent polarizability—it is independent of the impurity parameters  $\alpha_{i0}$  and  $M_i$ .

Equations (2.8) and (2.12) yield the following self-consistent equation for the impurity dipole moment arising from a given site configuration:

$$\mu_i = \alpha_{i0} \mathcal{G} \cdot \mu_i \left( 1 + \alpha_{i0}^2 |\mathcal{G} \cdot \mu_i|^2 / M_i^2 \right)^{-1/2}. \quad (2.14)$$

Similarly, from equations (2.7) and (2.12), the energy of the impurity state is

$$W_i = \frac{1}{2} \Delta \epsilon_i \left[ 1 - \left( 1 + \alpha_{i0}^2 |\mathcal{G} \cdot \mu_i|^2 / M_i^2 \right)^{1/2} \right]. \quad (2.15)$$

Equation (2.14) can be rewritten as an eigenvector-eigenvalue problem:

$$\mathcal{G} \cdot \mu_i = \frac{(1 + \alpha_{i0}^2 |\mathcal{G} \cdot \mu_i|^2 / M_i^2)^{1/2}}{\alpha_{i0}} \mu_i = \lambda \mu_i \quad (2.16)$$

where  $\lambda$  is one of the three eigenvalues of  $\mathcal{G}$ . Equation (2.16) always possesses the trivial solution

$$\mu_i = 0 \quad W_i = 0 \quad (2.17)$$

i.e. the zero-energy non-dipolar state of the impurity. If  $\alpha_{i0}\lambda > 1$ , however, then there is also a dipolar solution

$$\frac{|\mu_i|^2}{M_i^2} = 1 - \frac{1}{\alpha_{i0}^2 \lambda^2} \quad (2.18)$$

(where we have used the second equality of (2.16)), with energy

$$W_i = \frac{1}{2} \Delta \epsilon_i (1 - \alpha_{i0} \lambda). \quad (2.19)$$

In the dipolar phase, there are also non-zero contributions to the total energy of the system from the Hartree eigenvalues of the solvent atoms, and from the classical term of (2.1). It can be shown that these contributions amount to  $(\Delta \epsilon_i / 4) [\alpha_{i0} \lambda - (\alpha_{i0} \lambda)^{-1}]$  which, when added to (2.19), imply that the total energy of the system in the dipolar phase is negative. We conclude that the dipolar impurity state, when it exists, is stable with respect to the zero-energy non-dipolar state.

Thus, provided  $\alpha_{i0}\lambda > 1$  in each case, the lowest-energy solution arising from the Hartree Hamiltonian yields three self-consistent solutions for the impurity dipole moment, corresponding to the three eigenvalues of  $\mathcal{G}$ . For the large majority of site configurations, the three eigenvalues of  $\mathcal{G}$  are distinct. The ground-state solution then corresponds to the largest eigenvalue,  $\lambda_{\max}$ , since this gives the lowest energy (and also the largest impurity dipole moment). The impurity dipole moment is also of well defined magnitude and orientation. If, on the other hand, the largest eigenvalue is doubly or triply degenerate then, although the magnitude of  $\mu_i$  remains well defined, its orientation is to some extent arbitrary.

For a given configuration of sites, therefore, if  $\alpha_{i0}\lambda_{\max} < 1$  then the impurity atom is non-dipolar; and if  $\alpha_{i0}\lambda_{\max} > 1$  then the impurity has a dipole moment of magnitude given by (2.18) (with  $\lambda = \lambda_{\max}$ ) and usually of well defined orientation. Note that this result follows from the Hartree Hamiltonian for the model impurity system, with no further approximations introduced. In I, the dipolar EI phase predicted by the Hartree approximation was found to be in good agreement with the results of the pairing theory for a crystalline system, and we may therefore have confidence in the present results. In a fluid or disordered solid, however, we must go further and consider the ensemble of possible site configurations. Because of the assumed isotropy of the system, the ensemble average of  $\mu_i$  is zero, since for every configuration that yields a particular dipole moment, there is an equally weighted configuration that yields the opposite dipole moment. The average magnitude of  $\mu_i$  may, however, be non-zero.

Different site configurations are weighted, via the Boltzmann factor, by the potential energy of the configuration. This consists of two parts: the dipolar interaction energy arising from the electronic structure that we are calculating, and some reference potential (assumed to be spherically symmetric) that includes all other interactions. The dipolar interaction energy is non-zero only in the EI phase, where the impurity and its surrounding solvent atoms have non-zero dipole moments. We will, however, neglect entirely this contribution



to the potential energy; this can be shown to be consistent with the later restriction to linear theories. We thus assume different configurations to be weighted solely by the reference potential, which is of course independent of the magnitude of the dipole moments we wish to evaluate.

The problem is therefore to calculate the ensemble average of the magnitude of the impurity dipole moment, with different configurations weighted by the chosen reference potential. If  $f(\lambda_{\max})$  denotes the distribution function of  $\lambda_{\max}$  arising from the ensemble of site configurations, then the average magnitude of the impurity dipole moment can be written

$$\frac{\langle |\mu_i| \rangle}{M_i} = \int_{1/\alpha_{i0}}^{\infty} d\lambda_{\max} f(\lambda_{\max}) \left( 1 - \frac{1}{\alpha_{i0}^2 \lambda_{\max}^2} \right)^{1/2}. \quad (2.20)$$

Here, the lower limit of the integration corresponds to the limit of acceptability of the dipolar solution (2.18). If  $f(\lambda_{\max})$  is zero for all  $\lambda_{\max}$  above  $1/\alpha_{i0}$ , then clearly  $\langle |\mu_i| \rangle = 0$  and we have a normal insulating phase. Conversely, if  $f(\lambda_{\max})$  is non-zero for some  $\lambda_{\max}$  above  $1/\alpha_{i0}$ , i.e. some configurations give rise to an impurity dipole moment, then we have a dipolar EI phase.

To evaluate (2.20), we require a knowledge of  $f(\lambda_{\max})$ . This is clearly a formidable problem, and so we here adopt an alternative approximate approach. Instead of considering the eigenvalues of  $\mathcal{G}$  for the ensemble of configurations, we consider the eigenvalues of the ensemble average of  $\mathcal{G}$ :

$$\mathbf{G} = G\mathbf{I} = \langle \mathcal{G} \rangle \quad (2.21)$$

where  $\mathbf{I}$  is the identity matrix. This is clearly a mean field approximation.  $\mathbf{G}$  is isotropic, and trivially possesses a triply degenerate eigenvalue equal to  $G$ . The mean field approximation thus corresponds to replacing in (2.18) and (2.19) the eigenvalues of  $\mathcal{G}$ , namely  $\lambda$ , by the eigenvalue of  $\mathbf{G}$ , namely  $G$ . Because of the triple degeneracy of the eigenvalue of  $\mathbf{G}$ , the orientation of the predicted dipole moment  $\mu_i$  is completely arbitrary.

The mean field approximation is equivalent to assuming  $f(\lambda_{\max}) = \delta(\lambda_{\max} - G)$ , where  $\delta(x)$  is the Dirac delta function. Since  $G$  is likely to be less than a typical value of  $\lambda_{\max}$  (the largest of the three eigenvalues of  $\mathcal{G}$ ), we expect the mean field approximation to underestimate the occurrence of a dipolar EI phase. Furthermore, fluctuations in  $\lambda_{\max}$  are neglected, again leading to an underestimation of the occurrence of an EI phase, since when a normal insulating phase is predicted by the mean field theory, there might in fact be a fraction of configurations that give rise to an impurity dipole moment. Conversely, when an EI phase is predicted, the strength of the impurity dipole moment may be overestimated, since there might be a fraction of configurations that does not give rise to an impurity dipole moment. The dipolar EI phase is thus likely to occur over a wider range of system parameters, and the impurity dipole moment in the EI phase evolve more gradually, than the mean field theory would predict.

Explicitly, the mean field solution is as follows. When  $\alpha_{i0}G < 1$ , the only solution is

$$\mu_i = 0 \quad W_i = 0 \quad (2.22)$$

i.e. the zero-energy non-dipolar state of the impurity. When  $\alpha_{i0}G > 1$ , however, there is also a dipolar solution

$$\frac{|\mu_i|^2}{M_i^2} = 1 - \frac{1}{\alpha_{i0}^2 G^2} \quad W_i = \frac{1}{2} \Delta \epsilon_i (1 - \alpha_{i0} G) \quad (2.23)$$

and this solution is energetically stable with respect to the non-dipolar solution. The central quantity is clearly the average reaction field factor,  $G$ , which depends solely on the properties of the solvent. In particular,  $G$  increases with both solvent density and solvent polarizability.

The mean field approximation is equivalent to replacing  $\mathcal{G}$  in (2.14) by its ensemble average  $\mathbf{G} = G\mathbf{I}$ . With this replacement, (2.14) provides a self-consistency relation for  $\mu_i$  in terms of the impurity parameters,  $\alpha_{i0}$  and  $M_i$ , and the average reaction field factor,  $\mathbf{G}$ . This relation is of precisely the form obtained by Logan in his mean field theory of the dipolar EI phase of matrix-bound impurities (see (3.15) of [2] in the limit  $\beta \rightarrow \infty$ ), where continuum dielectric theory was used to obtain an expression for  $\mathbf{G}$  in terms of the density and polarizability of the solvent atoms. In contrast, from (2.13) and (2.21), we have here a prescription for a microscopic calculation of  $\mathbf{G}$ .

### 2.3. Linear theories

To use the mean field results, (2.22) and (2.23), we need to evaluate the average reaction field factor  $G$ . In this subsection, we consider the microscopic calculation of  $G$  in more detail, and for a particular class of approximate theories. From (2.13) and (2.21), we write

$$\mathbf{G} = \sum_{s=2}^N \rho^{s-1} \int \cdots \int g_s(i, 2 \dots s) G_s(i, 2 \dots s) d(2) \dots d(s). \quad (2.24)$$

Here,  $\rho = N/V$  is the number density of solvent sites, and  $g_s(i, 2 \dots s)$  is the normalized  $s$ -particle distribution function appropriate to the reference potential, which characterizes the ensemble average. The term  $G_s(i, 2 \dots s)$  stands for the sum of all terms contributing to  $\mathcal{G}$  that involve exactly  $s$  sites. Each term on the right-hand side of (2.24) can be represented in terms of composite graphs consisting of  $s$  points and two types of connectors. First, there may be connectors from the  $g_s(i, 2 \dots s)$  function, representing spatial correlations arising from the average over the reference system. Second, there is a continuous and directed chain of  $\mathbf{T}_{jk}$  bonds, representing a term in  $G_s(i, 2 \dots s)$ . The chain starts and ends at the impurity site  $i$ , touches each of the  $s$  points at least once, but does not visit  $i$  *en route*. A factor of  $\alpha_0$  is associated with each interior stage of the chain, where a stage is defined as a contact of the  $\mathbf{T}$ -chain with a point, and a factor of unity is associated with each end stage at  $i$ . The impurity site  $i$  is not integrated over and is termed a root point (RP). All solvent sites are integrated over and are field points (FP); with each FP is associated a factor of  $\rho$ .

The graphs contributing to  $\mathbf{G}$  may be analysed using the graph-theoretical methods introduced by Wertheim in his work [31] on non-polar polarizable fluids. The reader is referred to Wertheim's work for details of these methods, and here we merely summarize the procedure. The graphs contributing to  $\mathbf{G}$  are renormalized by the elimination of 2-articulation points (2-AP) (we use the modified terminology of [32]), and the consequent replacement of  $\alpha_0$  by a renormalized solvent polarizability,  $\alpha$ , at each interior stage.  $\mathbf{G}$  is then the sum of all composite graphs with RP  $i$ , at least one FP with each of which is associated a factor of  $\rho$ , connectors from  $g_s(i, 2 \dots s)$ , a single  $\mathbf{T}$ -bond chain beginning and ending at  $i$  for which  $i$  is not an interior stage, no 2-AP, and a factor of  $\alpha$  associated with each interior stage. The renormalized solvent polarizability is itself given by an expansion in renormalized (free of 2-AP) composite graphs, for which all points are solvent sites. More specifically,  $\alpha$  is given by precisely the prescription given above for  $\mathbf{G}$ , with the important difference that the RP is a solvent site and may be an interior stage of the  $\mathbf{T}$ -bond chain.

To make further progress in the analysis of  $\mathbf{G}$ , we must develop suitable approximate theories, by retaining only a subset of the most relevant graphs. Stabilization of the impurity dipole by the solvent is likely to be favoured by high solvent densities, and so we must

retain graphs in all powers of  $\rho$ . The subset of graphs that appear with the  $n$ th power of  $\rho$ , contains graphs in  $\alpha^n, \alpha^{n+1}$ , etc. Since we have supposed the solvent polarizability to be low,  $\alpha$  is also likely to be low, and the dominant contribution is likely to be from the graphs in  $\alpha^n$ . We therefore make the approximation of neglecting all graphs except those for which  $\alpha$  appears to the same power as  $\rho$ . This, in fact, corresponds to assuming a linear or single-site theory, for which only one stage is associated with each solvent site. The graphs contributing to  $\mathbf{G}$  now consist of a  $\mathbf{T}$ -bond chain from  $i$  to  $i$ , which touches each FP once only, with additional connectors arising from the reference  $s$ -particle distribution function,  $g_s(i, 2 \dots s)$ . Different linear theories correspond to different approximations for the latter connectors.

Within a linear theory,  $\alpha \mathbf{l}$  is given by  $\alpha_0 \mathbf{l}$  plus the sum of all renormalized composite graphs with one, two ... 'petals'. Each petal consists of a  $\mathbf{T}$ -bond chain that begins and ends at the RP, touching each FP once only, and with additional connectors arising from  $g_s(i, 2 \dots s)$ . A simple comparison of the graphs involved shows that for linear theories (and only for linear theories), and considered as a function of the  $g_s(i, 2 \dots s)$  connectors,  $\alpha$  is related to  $G$  by

$$\alpha = \alpha_0(1 - G\alpha_0)^{-1} \quad (2.25)$$

where  $G \equiv G(\alpha)$  is a function of the renormalized solvent polarizability, but is independent of the impurity parameters. One route to the calculation of  $G$  is thus via available microscopic theories of  $\alpha$ . This connection will be developed further in a subsequent paper, in which we will consider some explicit examples.

In addition to the work of Wertheim [31] mentioned above, there have also been studies of the renormalized polarizability of non-polar polarizable fluids within the so-called fluctuating-polarizability model [33–35]. For the cases considered, the results obtained are identical to those of Wertheim. A particularly useful result was obtained by Pratt [33] who showed that, for linear theories, the renormalized polarizability is given by

$$\alpha = \alpha_0 [1 + (2\alpha_0/3\alpha)\langle\beta U/N\rangle_{\bar{p}}]^{-1} \quad (2.26)$$

where  $\beta = (kT)^{-1}$  and  $\langle U/N \rangle_{\bar{p}}$  is the dipolar part of the internal energy per particle of a fluid composed of non-polarizable molecules with permanent dipole moment  $\bar{p} = (3\alpha/\beta)^{1/2}$ . Comparing (2.25) and (2.26), we identify

$$G = -(2/3\alpha)\langle\beta U/N\rangle_{\bar{p}}. \quad (2.27)$$

Many years ago, Onsager [36] discussed the lower bound of the electrostatic energy of a system of particles, each of which possesses an impenetrable spherical core of diameter  $\sigma$ . For a system of dipolar non-polarizable particles, his results translate into the fact that the quantity  $\langle U/N \rangle_{\bar{p}}$  has a lower bound equal to  $-4\bar{p}^2/\sigma^3$ . Using (2.27), and relating  $\bar{p}$  to the renormalized polarizability  $\alpha$  as above,  $G$  consequently satisfies the inequality

$$G \leq 8/\sigma^3. \quad (2.28)$$

In applying this inequality to the present situation, we have assumed that the solute atom and all solvent atoms have identical hard spherical cores of diameter  $\sigma$ . When this is true, the saturation of  $G$  clearly implies an upper limit to the magnitude of the impurity dipole moment (see (2.23)). Indeed, if  $\alpha_{i0}\sigma^{-3} < 1/8$  then no impurity dipole is possible within a linear theory.

As explained above, within linear theories the  $\rho$  and  $\alpha$  dependence of  $G$  enters solely via the combination  $\rho\alpha$  (except for the weaker  $\rho$  dependence of the many-particle reference distribution functions). To lowest order in  $\rho\alpha$ ,  $G$  is given by

$$G = \rho\alpha \int d\mathbf{R} g_2(R) \frac{1}{3} \text{Tr}(\mathbf{T}(\mathbf{R}) \cdot \mathbf{T}(-\mathbf{R})) + O[(\rho\alpha)^2] \\ = 8\pi\rho\alpha \int_0^\infty dR R^{-4} g_2(R) + O[(\rho\alpha)^2] \quad (2.29)$$

where  $g_2(R)$  is the pair distribution function appropriate to the reference potential.

### 3. Dynamic response

#### 3.1. Normal insulating phase

In this section, we consider the dynamic response of the model system to an oscillatory electric field. In particular, we are interested in how the transition to a dipolar EI phase, discussed above, is reflected in the optical absorption of the system. We consider first the general model system described in section 2.1 in the normal insulating regime, turning afterwards to the example of an impurity system. In the following subsection, we examine the dynamic response of the impurity system in the EI phase.

We know from linear response theory that the dipole moment induced on any atom  $i$ , by an oscillatory local electric field,  $\mathbf{E}_i(\omega)$ , is given to linear order in the local field by

$$\boldsymbol{\mu}_i(\omega) = \alpha_{i0}(\omega) \mathbf{E}_i(\omega) \quad (3.1)$$

where the frequency-dependent polarizability,  $\alpha_{i0}(\omega)$ , (assumed isotropic) is expressed in terms of the energy levels of the atom. For the model system of section 2.1,  $\alpha_{i0}(\omega)$  is of the form

$$\alpha_{i0}(\omega) = \alpha_{i0} [1 - \hbar^2(\omega + i\eta)^2 / \Delta\epsilon_i^2]^{-1} \quad (3.2)$$

where  $\alpha_{i0}$  is the static polarizability of site  $i$ , and  $\eta$  is a positive infinitesimal. At  $T = 0$ ,  $\alpha_{i0}$  is given by (2.9).

For an isolated atom, the local field,  $\mathbf{E}_i(\omega)$ , is simply the externally applied field,  $\mathbf{E}^{\text{ext}}(\omega)$ , and the optical absorption coefficient is proportional to  $\omega \text{Im}[\alpha_{i0}(\omega)]$ . The absorption spectrum thus consists of a delta function at the atomic transition frequency,  $\Delta\epsilon_i/\hbar$ . In the condensed phase, and for a given site centre-of-mass configuration, the local field is

$$\mathbf{E}_i(\omega) = \mathbf{E}^{\text{ext}}(\omega) + \sum_j \mathbf{T}_{ij} \cdot \boldsymbol{\mu}_j(\omega) \quad (3.3)$$

where  $\boldsymbol{\mu}_j(\omega)$  is the dipole moment induced on site  $j$ , directly and indirectly, by the external field. Taken together, (3.1) and (3.3) are formally equivalent to the Yvon-Kirkwood equations (2.10), with the static polarizability replaced by the dynamic polarizability,  $\alpha_{i0}(\omega)$ . With this replacement, the dynamic response of the condensed system can be obtained from the solution of the Yvon-Kirkwood equations.

Of particular interest is the optical absorption coefficient, which may be related to the imaginary part of a susceptibility function that includes both site-diagonal and off-diagonal components (see, for example, [37]). The site-diagonal component is, in fact,

the renormalized dynamic polarizability,  $\alpha_i(\omega)$ . Because of the isomorphism with the static Yvon-Kirkwood equations mentioned above,  $\alpha_i(\omega)$  is related to the bare dynamic polarizability,  $\alpha_{i0}(\omega)$ , in precisely the way that the renormalized static polarizability,  $\alpha_i$ , is related to the bare static polarizability,  $\alpha_{i0}$ . Thus, from theories of the renormalized static polarizability we may obtain the site-diagonal contribution to the absorption spectrum by simply replacing  $\alpha_{i0}$  with  $\alpha_{i0}(\omega)$ . The site-diagonal component is sufficient to obtain the frequency ranges in which absorption takes place, but the off-diagonal component is required in addition to obtain the correct lineshape. Here, we consider solely the former.

For a neat liquid, the renormalized dynamic polarizability was studied within the MSA by Høye and Olaussen [38], and within a Padé approximant theory by Chandler and co-workers [30]. Both groups found the imaginary part of the renormalized dynamic polarizability to be non-zero over a range of positive frequencies, the delta function absorption of the isolated atom being broadened into an absorption band. The states that give rise to the absorption band may be identified as Frenkel excitons [29]. As discussed earlier and in detail in I, a transition to the Frenkel EI phase occurs when the lowest-energy exciton state becomes degenerate with the ground state. In the present context, a transition occurs when the lower edge of the absorption band associated with the imaginary part of the renormalized dynamic polarizability reaches zero frequency. As mentioned in section 2.1, this is the criterion used in the work of Logan and Edwards [13].

For the impurity system of section 2.2, we expect the solvent atoms to give rise to an absorption band in the same manner as the neat liquid considered above. In general, the impurity atom gives rise to an absorption peak either inside or outside the absorption band of the solvent, but, for the systems that we are interested in, the impurity absorbs at a frequency or range of frequencies well below the solvent band. To calculate the impurity absorption, we require the renormalized dynamic polarizability of the impurity [30, 39]. Equation (2.25), which for linear theories relates the renormalized polarizability of a solvent atom to the average reaction field factor, also holds for the impurity atom in the normal insulating regime. In the dynamic case, with  $\alpha_{i0}$  replaced by  $\alpha_{i0}(\omega)$ , this relation is

$$\alpha_i(\omega) = \alpha_{i0}(\omega) [1 - G(\omega)\alpha_{i0}(\omega)]^{-1} \quad (3.4)$$

where  $G(\omega) \equiv G[\alpha(\omega)]$  is a function of the renormalized dynamic solvent polarizability.

For frequencies outside the solvent absorption band, where we have assumed the impurity absorption to occur,  $\alpha(\omega)$  and hence  $G(\omega)$  is real. Therefore, with  $\alpha_{i0}(\omega)$  given by (3.2), it is clear that  $\text{Im}[\alpha_i(\omega)]$  is a delta function at a frequency which is a zero of [30, 39]

$$\Delta\epsilon_i^2 [1 - G(\omega)\alpha_{i0}] - \hbar^2\omega^2. \quad (3.5)$$

Thus, the impurity has a delta function absorption spectrum at a frequency which is redshifted from  $\Delta\epsilon_i/\hbar$  as the solvent density, and hence  $G(\omega)$ , is increased from zero [30, 39].

There is a transition to the EI phase, and consequently the formation of a dipolar impurity atom, when the state giving rise to this absorption line becomes degenerate with the ground state, i.e. when the frequency of the impurity line becomes zero. Remembering that  $\alpha(\omega) = \alpha$  at  $\omega = 0$ , the condition that  $\omega = 0$  is a zero of (3.5) is

$$G\alpha_{i0} = 1 \quad (3.6)$$

where  $G \equiv G[\alpha]$ . This is precisely the condition for the transition to an EI phase found in section 2.2. We have thus derived the condition for an EI transition in an impurity system, within a linear mean field theory, in two distinct ways. In section 2.2, we found the

condition under which the Hartree Hamiltonian would support a dipolar solution. In this section, and in the spirit of the exciton theory of I, we have found the condition under which the lowest-lying excited state becomes degenerate with the ground state. It is gratifying that both approaches yield the same answer.

Experimentally, it is found that the absorption line of a dilute impurity in a liquid or glassy solvent is inhomogeneously broadened by the distribution of solvent environments (see e.g. [40]), and there have recently been many attempts to model this broadening theoretically [37, 41–46]. It is straightforward to show that the delta function absorption implied by (3.4) is a direct result of the use of a linear theory. Within a non-linear theory, a graphical analysis shows that  $\alpha_i(\omega)$  is given again by an equation of the form of (3.4), but with  $G(\omega)$  replaced by a quantity that is a function of  $\alpha_i(\omega)$  as well as  $\alpha(\omega)$ . Equation (3.4) thus becomes a self-consistency equation for  $\alpha_i(\omega)$ , which may have complex solutions over a range of frequencies, implying an absorption band *per se*. The need for a non-linear theory to obtain a broadened impurity line has also been pointed out by Chen and Stratt [37, 46]. Clearly, if a particular system exhibits significant inhomogeneous broadening, then a linear theory is inappropriate, and the above description of the EI instability must be improved.

In section 2.2, we showed that for a given site configuration the impurity is dipolar if  $\alpha_{i0}\lambda_{\max} > 1$ , where  $\lambda_{\max}$  is the largest eigenvalue of  $\mathcal{G}$ . If one goes through the above argument for the impurity absorption line for a given site configuration, then this criterion for the EI phase is again recovered. The equivalence of these two routes is therefore not an artifact of the linear mean field theory. Consideration of the ensemble of possible site configurations then leads to a distribution of impurity lines and consequently a distribution of transition criteria. For the special case of a linear mean field theory, we recover the scenario described above.

### 3.2. The EI phase

Within the EI phase, as discussed in section 2, it is essential to consider the non-linear response of the impurity to the local field, and thus (3.1) is inappropriate for the impurity. One can, however, consider the linear response of the impurity to the *change* in the local field,  $\Delta E_i(\omega)$ , resultant upon the application of an external field. The change in the dipole moment,  $\Delta \mu_i(\omega)$ , induced on the impurity is given to linear order in  $\Delta E_i(\omega)$  by

$$\Delta \mu_i(\omega) = \alpha_{i0}^{\text{EI}}(\omega) \cdot \Delta E_i(\omega) \quad (3.7)$$

where  $\alpha_{i0}^{\text{EI}}(\omega)$  (in general anisotropic) is a modified dynamic polarizability appropriate to the impurity in the dipolar EI phase. The latter is given from linear response theory in terms of the Hartree eigenstates of the impurity. In the EI phase, these differ from the states of the  $sp^3$  basis, and thus  $\alpha_{i0}^{\text{EI}}(\omega)$  differs from the gas phase quantity,  $\alpha_{i0}(\omega)$ .

As discussed in section 2.2, we assume that the solvent atoms respond linearly to the local field, even in the EI phase. This is equivalent to assuming that the bare dynamic polarizability of a solvent atom is unchanged in the EI phase. Thus, for all solvent atoms  $j$ , we have

$$\Delta \mu_j(\omega) = \alpha_0(\omega) \Delta E_j(\omega). \quad (3.8)$$

The change in the local field at the impurity site,  $\Delta E_i(\omega)$ , is given by the external field plus the change in the local field arising from the change in the solvent dipole moments

$$\Delta E_i(\omega) = E^{\text{ext}}(\omega) + \sum_j \mathbf{T}_{ij} \cdot \Delta \mu_j(\omega) \quad (3.9)$$

A similar equation holds for all solvent sites.

Equations (3.7)–(3.9) are formally equivalent to the Yvon–Kirkwood equations (2.10), and describe the linear response of the impurity,  $\Delta\mu_i(\omega)$ , arising directly and indirectly from the application of the external field  $E^{\text{ext}}(\omega)$ . With this equivalence, the dynamic response of the system in the EI phase can be obtained following the procedure of the previous subsection. The sole, but important, difference is that the impurity possesses a modified dynamic polarizability,  $\alpha_i^{\text{EI}}(\omega)$ , rather than the gas phase polarizability,  $\alpha_{i0}(\omega)$ , reflecting the fact that the impurity is in a dipolar state.

Following the procedure of section 3.1, the primary contribution to the impurity absorption comes from the imaginary part of the renormalized modified dynamic polarizability,  $\alpha_i^{\text{EI}}(\omega)$ , which, within a linear theory, is obtained from

$$\alpha_i^{\text{EI}}(\omega) = \alpha_{i0}^{\text{EI}}(\omega)[1 - G(\omega)\alpha_{i0}^{\text{EI}}(\omega)]^{-1}. \quad (3.10)$$

With the assumptions we have made above about the solvent,  $G(\omega) \equiv G[\alpha(\omega)]$  is the same function that appears in (3.4) for the normal insulating phase. The position of the impurity absorption line is determined by a pole of the right-hand side of (3.10), to locate which we need a form for  $\alpha_{i0}^{\text{EI}}(\omega)$ .

The term  $\alpha_{i0}^{\text{EI}}(\omega)$  has a set of mutually orthogonal principal axes, one of which lies parallel to the dipole moment of the EI phase. We denote the latter by  $\alpha_{i0\parallel}^{\text{EI}}(\omega)$ , and the two transverse components by  $\alpha_{i0\perp}^{\text{EI}}(\omega)$ . From (3.10), we obtain the corresponding components,  $\alpha_{i\parallel}^{\text{EI}}(\omega)$  and  $\alpha_{i\perp}^{\text{EI}}(\omega)$ , of  $\alpha_i^{\text{EI}}(\omega)$ . In fact, only  $\alpha_{i\parallel}^{\text{EI}}(\omega)$  is physically significant. It was shown in section 2.2 that the dipole moment predicted by the mean field theory has, in the absence of an external field, an arbitrary orientation. In the presence of an infinitesimal field, however, the dipole moment lies parallel to that field. Consequently, in switching on the external field  $E^{\text{ext}}(\omega)$  from an infinitesimal magnitude, keeping its orientation fixed, the dipole moment necessarily lies parallel to  $E^{\text{ext}}(\omega)$ , and hence only  $\alpha_{i\parallel}^{\text{EI}}(\omega)$  can be probed. If one calculates the transverse components, one finds that  $\alpha_{i\perp}^{\text{EI}}(0)$  is infinite in the EI phase, reflecting the infinite susceptibility of the impurity dipole with respect to changing its orientation to that of the field. In the following, we therefore only consider the parallel component,  $\alpha_{i\parallel}^{\text{EI}}(\omega)$ .

The solution of the Hartree Hamiltonian (2.1) in the absence of an external field yields for the impurity atom four eigenenergies,  $W_1$ – $W_4$ , and four corresponding eigenfunctions, given in terms of the local field,  $E_i$ . In section 2, we dealt solely with the lowest-energy state, the eigenenergy of which is given by (2.7), and the corresponding eigenfunction was used to determine the impurity dipole moment (2.8). To calculate the modified impurity polarizability, we must now consider virtual transitions between all four solutions. In terms of these solutions, linear response theory leads to the following expression for the modified dynamic polarizability of the impurity:

$$\alpha_{i0}^{\text{EI}}(\omega) = 2 \sum_f \frac{\mathcal{M}_{1f}\mathcal{M}_{f1}}{(W_f - W_1)} [1 - \hbar^2(\omega + i\eta)^2/(W_f - W_1)^2]^{-1}. \quad (3.11)$$

Here, 1 is the lowest-energy eigenstate, and  $f$  runs over the remaining three states. The term  $\mathcal{M}_{1f}$  is the transition dipole moment vector between states 1 and  $f$ , and is determined from the eigenfunctions of these states. In the normal insulating phase, states 1–4 are simply the  $s$  orbital and three  $p$ -orbitals of the basis, and (3.11) reduces to (3.2) with (2.9).

Equation (3.11) gives  $\alpha_{i0}^{\text{EI}}(\omega)$  in terms of the eigenenergies and eigenfunctions of the impurity, and hence in terms of the local field,  $E_i$ . The mean field theory of section 2.2 replaces  $E_i$  by  $G\mu_i$ , where  $G \equiv G[\alpha]$  is a function of the renormalized static polarizability

of the solvent, and  $\mu_i$  is given by (2.23). We thus write  $\alpha_{i0}^{\text{EI}}(\omega)$  in terms of  $G$ , from which it can be shown that

$$\alpha_{i0}^{\text{EI}}(\omega) = \frac{1}{\alpha_{i0}^2 G^3} [1 - \hbar^2(\omega + i\eta)^2 / (\Delta\epsilon_i \alpha_{i0} G)^2]^{-1}. \quad (3.12)$$

It can be seen that in the EI phase ( $\alpha_{i0} G > 1$ ),  $\alpha_{i0}^{\text{EI}}(0)$  is reduced with respect to the gas phase value  $\alpha_{i0}$ . Finally, from (3.10) and (3.12) it follows that

$$\alpha_{i\parallel}^{\text{EI}}(\omega) = [\alpha_{i0}^2 G^3 - \hbar^2(\omega + i\eta)^2 G / \Delta\epsilon_i^2 - G(\omega)]^{-1}. \quad (3.13)$$

Equation (3.13) is the desired expression for the parallel component of the renormalized modified polarizability of the impurity in terms of the average reaction field factor and the parameters of the impurity atom. The term  $\alpha_{i\parallel}^{\text{EI}}(\omega)$  has a pole at a frequency which is a zero of

$$\Delta\epsilon_i^2 [\alpha_{i0}^2 G^2 - G(\omega) / G] - \hbar^2 \omega^2 \quad (3.14)$$

and this is the frequency of the impurity absorption line in the EI phase. We see that (3.6) is recovered as the condition that  $\omega = 0$  is a zero of (3.14), i.e. (3.6) is also the criterion for the transition when the latter is approached from the EI phase. For  $\alpha_{i0} G > 1$ , i.e. within the EI phase, the absorption line moves again to positive frequencies.

We now summarize the behaviour of the lowest excited state of the system, which is responsible for the impurity absorption line, as the system is driven through the EI transition. As the transition is approached from the normal insulating phase, the excited state that gives rise to the absorption line is reduced in energy towards the ground state. There is, however, no mixing between them, and the ground state is pure s-like. At the transition, the excited state becomes degenerate with the ground state, there is mixing, and a new sp-hybridized ground state is formed. As the system enters the EI phase, there is continued mixing between the new ground state and the lowest excited state, pushing these states apart in energy and increasing the ground-state dipole moment.

These changes are reflected in the frequency of the impurity absorption line, as determined by equations (3.5) and (3.14) and shown schematically in figure 1. Initially, the line is redshifted from the transition frequency,  $\Delta\epsilon_i/\hbar$ , of the isolated atom. Over a relatively narrow range of solvent density about the transition density, the line drops to zero frequency, and then moves again to positive frequencies. For very high densities, the line is blue-shifted from the isolated atom frequency, and tends towards the value  $\Delta\epsilon_i \alpha_{i0} G$  representing a transition from the lowest-energy to the highest-energy Hartree eigenstate of the impurity. Also shown in figure 1 is the bottom of the absorption band associated with the solvent. The solvent band broadens with increasing solvent density, and at a high density the impurity line may merge into the band.

The behaviour of the excited state associated with the impurity is also reflected in the static dielectric susceptibility of the impurity to the applied field. We expect the dominant contribution to come from the site-diagonal part. From (3.4) with  $\omega = 0$ , we have

$$\alpha_i = \alpha_{i0} (1 - G\alpha_{i0})^{-1} \quad G\alpha_{i0} < 1. \quad (3.15)$$

Clearly, the susceptibility diverges with a mean field exponent of one as the transition is approached from the normal insulating phase. Conversely, from (3.13):

$$\alpha_{i\parallel}^{\text{EI}} = \frac{1}{G} (\alpha_{i0}^2 G^2 - 1)^{-1} \quad G\alpha_{i0} > 1. \quad (3.16)$$

Thus, the susceptibility also diverges with a mean field exponent of 1 as the transition is approached from the EI phase. This divergence of the static susceptibility results from the degeneracy of the ground and first excited states at the transition. Equations (3.15) and (3.16) have precisely the forms found by Logan [2].



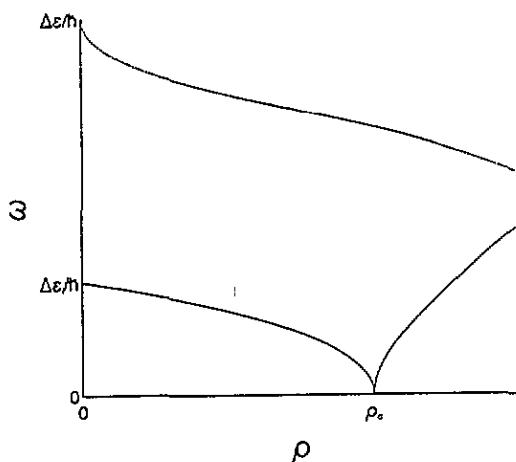


Figure 1. Schematic illustration of the variation with solvent density of the impurity absorption line (full curve).  $\Delta\epsilon_i/\hbar$  ( $\Delta\epsilon/\hbar$ ) is the gas-phase transition frequency of the impurity (solvent), and  $\rho_c$  is the density of the transition to a dipolar EI phase. Also shown (broken curve) is the lower edge of the solvent absorption band.

#### 4. Summary and discussion

In this paper, we have extended the Hartree approximation introduced in I to the case of spatially disordered systems. In particular, we have studied the case of an impurity at infinite dilution in a solvent, a situation relevant to several experimental systems. Taking into account the ensemble of site configurations via a mean field approximation, we obtained a self-consistency equation for the dipole moment of the impurity atom in terms of the average reaction field factor,  $G$ , non-zero solutions to which indicate the occurrence of a dipolar Frenkel EI phase. This self-consistency equation has precisely the form obtained by Logan [2], but in contrast to the continuum dielectric theory employed by Logan, the present derivation allows a microscopic calculation of  $G$ .

In section 3, we examined the linear response of the model system to an external oscillating electric field, and located the lowest excited state associated with the impurity. The transition to a dipolar EI phase, as predicted by the Hartree approach, was found to coincide with the impurity excited state becoming degenerate with the ground state. We thus make contact with the viewpoint of the exciton theory of I, by asserting that the transition is driven by the admixture of the excited state into the ground state, consequent upon the latter becoming degenerate with the ground state.

We now discuss how the picture of the dipolar Frenkel EI phase developed in this paper would be reflected experimentally. The evolution of the impurity excited state, as described in section 3, is reflected in the frequency of the impurity absorption line. This would, if experimentally feasible, provide the most direct method of observing the transition to an EI phase, since it shows explicitly the degeneracy with the ground state at the transition of a formerly excited state. In practice, the observation of this phenomenon is more difficult because of inhomogeneous broadening of the impurity line. The transition, when there is broadening, occurs when the lower edge of the impurity band becomes degenerate with the ground state, and the location of a lower band edge is necessarily more difficult. Despite this, the variation with solvent density of the maximum of the impurity band should be clearly non-monotonic, decreasing (increasing) with increasing density in the normal (EI) phase, as shown in figure 1.

Associated with the behaviour of the impurity excited state is the divergence of the static dielectric susceptibility of the impurity (see section 3.2), and hence the static dielectric constant of the sample, at the transition. Following the discussion of Logan [2], this divergence should, in the majority of cases, occur over an observable range.

Although not explicitly dealt with in the present paper, magnetic resonance experiments provide another probe of the dipolar EI phase. As the system undergoes a transition from a normal insulating phase to an EI phase, the impurity changes from a pure *s* state to an *sp*-hybridized state (see above). Consequently, the electron density at the impurity nucleus is reduced in the EI phase, and this will be reflected in a reduced hyperfine interaction between the electron and nucleus. (We note that the double excitation terms of the model Hamiltonian in fact mix some *p* character into the ground state for all non-zero densities (see I). This effect is neglected in the Hartree approximation, but is small in comparison with the changes associated with the EI transition.) The observation in ESR experiments of a reduction in the hyperfine interaction was, in fact, what prompted Chenier and co-workers [3] to speculate on the formation of dipolar states of Cu, Ag and Au in alkali halide matrices. For the alkali metals in many amine and ether solvents, ESR experiments indicate an electron density at the alkali nucleus intermediate between that of the gas phase atom and that of the fully ionized atom. This is usually taken to indicate an *s* state, which is more diffuse than that of the gas phase atom [47,48], but the formation of a dipolar state is a further possibility. We discuss the situation in alkali metal/amine systems further in a following paper.

In this paper, we have analysed the behaviour of the dipolar EI phase that occurs in the model system introduced in I, but we must of course bear in mind the limitations of the model. A number of these were discussed in I, to which the reader is referred, and here we mention only a few specific to impurity systems.

In some systems, most notably alkali metals at low concentration in liquid ammonia, the valence electron of the impurity dissociates completely from the impurity, occupying a cavity in the solvent. The solvated electron is then a species distinct from the solvated impurity ion. The tight-binding description we have employed, with basis orbitals associated with atomic sites, is clearly incapable of modelling such a possibility. Less drastically, interaction with the solvent may cause the impurity excitation to be of larger radius than the Frenkel excitation we have assumed.

Further, we have only considered a single impurity atom. As the concentration of the impurity species is increased, however, interactions between different impurity atoms become significant. With the present model Hamiltonian, the principal effect is likely to be a broadening of the impurity excited state into a band, due to resonant transfer of the excitation between impurities. The transition to a Frenkel EI phase, with the formation of significant dipole moments on all impurity sites, occurs when the lower edge of the impurity band becomes degenerate with the ground state. As discussed in I, however, a number of terms were neglected in constructing the model Hamiltonian, of which the one-electron transfer matrix elements, which allow electrons to hop between sites, are expected to be the most significant. Transfer matrix elements connecting different impurity sites will, as the impurity concentration increases, cause the Frenkel EI phase to evolve into a Mott-Wannier EI phase, followed by a metallic phase via a Mott unbinding transition [49].

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