

Exciton transport and degenerate four wave mixing in topologically disordered systems

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The static and dynamical properties of excitons in a lattice with a random distribution of polarizable atoms are studied using Green's function techniques. Exciton transport is related to the configurationally averaged particle-hole Green's function which is calculated using the ladder diagram approximation. Degenerate four wave mixing (D4WM) using resonant pump beams and an off resonant probe is shown to provide a direct probe for exciton transport. A disorder induced extra resonance is predicted whose width is proportional to the exciton diffusion coefficient. Numerical calculations are presented for the diffusion coefficient and the D4WM signal as the excitation energy is tuned across the exciton band.

I. INTRODUCTION

The static and dynamical properties of excitons in disordered systems may be studied using Green's function techniques. The density of states is related to the configurationally averaged single particle ($1-p$) Green's function, while transport properties are related to the configurationally averaged particle-hole ($p-h$) Green's function. For a lattice where the atoms have a random transition frequency (diagonal disorder), the configurationally averaged $1-p$ Green's function has been well studied by methods such as the coherent potential approximation (CPA).¹ Diagrammatic methods² as well as the replica method combined with the mean spherical approximation (MSA)³⁻⁵ have been applied recently to calculate this Green's function in liquids. Quantum transport in a diagonally disordered model was studied by calculating the configurationally averaged $p-h$ Green's function using diagrammatic methods.⁶⁻⁹ These calculations show the appearance of a mobility edge and Anderson localization.

Loring and Mukamel¹⁰ have developed a self-consistent procedure [the effective dephasing approximation (EDA)] for calculating exciton transport and quantum localization in disordered systems. The approach is based on the Liouville space Green's function which is equivalent to the particle-hole ($p-h$) Green's function in Hilbert space.

The optical response of excitons in a disordered medium can also be studied using Green's function techniques. The linear absorption line shape is related to the configurationally averaged $1-p$ Green's function. Using the MSA to calculate the configurationally averaged $1-p$ Green's function of a Drude liquid, Cheng and Stratt³ obtained the linear absorption line shape. Loring and Mukamel^{10,11} showed that the transient grating signal of a crystal is related to exciton transport which is determined by the $p-h$ Green's function. They studied the nonlinear susceptibility $\chi^{(3)}$ for the Haken-Strobl model¹¹ and predicted that a narrow resonance that can show up in degenerate four wave mixing (D4WM) is related to the Fourier transform of the transient grating signal amplitude and can be used as a simple and direct probe for exciton transport. A

limitation of that treatment is that it contains a Green's function integrated over the entire exciton band and thus does not provide any information regarding the variation of the nature of the states across the exciton band. In this article, we generalize the method of Loring and Mukamel and develop an energy dependent self-consistent theory for the $p-h$ Green's function. The method is applied to a lattice with randomly distributed polarizable atoms, and we find that the degenerate four wave mixing (D4WM) signal is determined by the configurationally averaged $p-h$ Green's function [see Eq. (30)]. Thus the D4WM experiment can be used as a probe for exciton transport.

We use the coherent potential approximation (CPA)¹ to calculate the $1-p$ Green's function and then make the ladder diagram approximation^{8,9} to calculate the $p-h$ Green's function. Numerical calculations for the density of states, the energy dependent diffusion coefficient, and the D4WM signal are presented.

II. 1-P AND P-H GREEN'S FUNCTIONS FOR EXCITON DYNAMICS

Consider a lattice with M sites, N of which are occupied by hydrogen-like atoms, each having one $1s$ orbital and three $2p$ orbitals. We denote the fraction of occupied sites by $c \equiv N/M$. To describe this system, we will adopt the lattice Hamiltonian

$$H = \sum_{r,\alpha} \epsilon_{r\alpha} B_{r\alpha}^+ B_{r\alpha} + \sum_{r \neq r', \alpha, \beta} J_{\alpha\beta}(r-r') B_{r\alpha}^+ B_{r'\beta}. \quad (1)$$

Here $\alpha, \beta = p_x, p_y, p_z$ denote the three excited p orbitals. The operators $B_{r\alpha}^+$ and $B_{r\alpha}$ are the creation and annihilation operator of exciton at site r with polarization α ,

$$B_{r\alpha}^+ |0\rangle = |\alpha\rangle. \quad (2)$$

Here $|0\rangle$ denotes the ground state (i.e., all sites are in their ground states) and $|\alpha\rangle$ denotes the state in which site r is excited with polarization α and all other sites are in their ground states. In Eq. (1), r and r' run over all lattice sites. Note that the Hamiltonian (1) conserves the number of excitons. This is the result of the Heitler-London approximation.¹² $\epsilon_{r\alpha}$ is the excitation energy of site r which is

equal to Ω (the energy gap between s and p orbitals) when site \mathbf{r} is occupied and is equal to ϵ_1 when site \mathbf{r} is not occupied by the atom. Therefore $\epsilon_{r\alpha}$ is a random variable with a probability distribution of binary form

$$p(\epsilon_{r\alpha}) = c\delta(\epsilon_{r\alpha} - \Omega) + (1 - c)\delta(\epsilon_{r\alpha} - \epsilon_1). \quad (3)$$

By taking the limit $\epsilon_1 \rightarrow \infty$, we make the unoccupied sites inaccessible and the Hamiltonian then represents our system. Using this representation, the topological disorder is mapped into a diagonal disorder with binary distribution of excitation energy. We can therefore use the various methods of calculating the Green's function for a diagonally disordered crystal^{6-9,13,14} to treat the topologically disordered model.

In our model, each site can carry at most one exciton. Considering the action of $B_{r\alpha}$ and $B_{r\alpha}^+$ on the complete basis set $|0\rangle$, $|r p_x\rangle$, $|r p_y\rangle$, $|r p_z\rangle$, we can derive the commutation relation

$$\begin{aligned} [B_{r\alpha}, B_{r'\beta}^+] &= \delta_{r,r'}(\delta_{\alpha\beta} - B_{r\beta}^+ B_{r\alpha} - \delta_{\alpha\beta} \hat{n}_r), \\ [B_{r\alpha}, B_{r'\beta}] &= [B_{r\alpha}^+, B_{r'\beta}^+] = 0, \end{aligned} \quad (4)$$

with

$$\hat{n}_r = \sum_{\sigma} B_{r\sigma}^+ B_{r\sigma}.$$

Here \hat{n}_r is the exciton number operator at site \mathbf{r} . Note that $B_{r\alpha}$ and $B_{r'\beta}^+$ commute when they act on different sites and thus behave like bosons. However, when they act on the same site, we find nonlinear corrections to this Boson character.

In Eq. (1), $J_{\alpha\beta}(\mathbf{r})$ is the dipole-dipole interaction tensor

$$J_{\alpha\beta}(\mathbf{r}) = \mu^2 \frac{\delta_{\alpha\beta} r^2 - 3r_{\alpha} r_{\beta}}{r^5}, \quad (5)$$

where μ is the transition dipole moment. For simplicity, we hereafter take $\mu = 1$.

We next introduce the single particle (1- p) Green's function $G_{\alpha\beta}(\mathbf{r}, \mathbf{r}', z)$,

$$G_{\alpha\beta}(\mathbf{r}, \mathbf{r}', z) = \langle r\alpha | \frac{1}{z - H} | r'\beta \rangle, \quad (6)$$

where z is a complex number. The exciton density of states is proportional to the imaginary part of the trace of the configurationally averaged 1- p Green's function. We have

$$\begin{aligned} N(E) &\equiv \frac{1}{3N} \overline{\text{Tr}[\delta(E - H)]} \\ &= -\frac{1}{3N\pi} \text{Im} \sum_{r,\alpha} \bar{G}_{\alpha\alpha}(\mathbf{r}, \mathbf{r}, E + i0). \end{aligned} \quad (7)$$

We use an overbar to denote the average over configurations in this paper.

We next look at the transport properties of the single exciton states. Let $\rho_{\alpha\beta}(\mathbf{r}, \mathbf{r}', t)$ denote the matrix elements of the density operator $\hat{\rho}(t)$ in the single exciton subspace

$$\hat{\rho}(t) = \sum_{r,\mathbf{r}',\alpha,\beta} \rho_{\alpha\beta}(\mathbf{r}, \mathbf{r}', t) |r\alpha\rangle \langle r'\beta|. \quad (8)$$

The evolution of the density matrix is given by

$$\rho_{\alpha\sigma}(\mathbf{r}_1, \mathbf{r}_3, t) = \sum_{\beta\gamma\mathbf{r}_2\mathbf{r}_4} \mathcal{G}_{\alpha\beta}^{\sigma\gamma}(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2, \mathbf{r}_4, t) \rho_{\beta\gamma}(\mathbf{r}_2, \mathbf{r}_4, 0), \quad (9)$$

$$\mathcal{G}_{\alpha\beta}^{\sigma\gamma}(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2, \mathbf{r}_4, t) = \langle r_1\alpha | e^{-iHt} | r_2\beta \rangle \langle r_4\gamma | e^{iHt} | r_3\sigma \rangle. \quad (10)$$

Here \mathcal{G} is the propagator of the density matrix. We now introduce the configurationally averaged particle-hole (p - h) Green's function $\phi_{\alpha\beta}^{\sigma\gamma}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, z_1, z_2)$ as

$$\phi_{\alpha\beta}^{\sigma\gamma}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, z_1, z_2) \equiv \overline{G_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, z_1) G_{\gamma\sigma}(\mathbf{r}_4, \mathbf{r}_3, z_2)}. \quad (11)$$

Here z_1, z_2 are complex numbers. The configurationally averaged density matrix propagator is then given by

$$\begin{aligned} \mathcal{G}_{\alpha\beta}^{\sigma\gamma}(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2, \mathbf{r}_4, t) &= \frac{1}{4\pi^2} \int d\omega e^{-i\omega t} \int dE \\ &\times \phi_{\alpha\beta}^{\sigma\gamma}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, E + \frac{\omega}{2} + i0, E - \frac{\omega}{2} - i0). \end{aligned} \quad (12)$$

Here $+i0$ ($-i0$) denote the retarded (advanced) Green's function. In order to study the transport properties of the system, we need to calculate the configurationally averaged p - h Green's function $\phi_{\alpha\beta}^{\sigma\gamma}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, z_1, z_2)$, which describes the complete propagation of the exciton's density matrix. For many applications, we need consider only the diagonal elements of the density matrix (i.e., populations). This corresponds to adopting the master equation (rather than the complete phase space) level of description. To that end, we introduce the conditional probability of an exciton to move to site \mathbf{r}_1 with polarization α given that it is initially at \mathbf{r}_2 with polarization β ,

$$\begin{aligned} \mathcal{P}_{\alpha\beta}(\mathbf{r}_1 - \mathbf{r}_2, t) &\equiv \frac{1}{c} \overline{\langle r_1\alpha | e^{-iHt} | r_2\beta \rangle \langle r_2\beta | e^{iHt} | r_1\alpha \rangle} \\ &\equiv \frac{1}{c} \mathcal{G}_{\alpha\beta}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_2, t). \end{aligned} \quad (13)$$

From Eq. (12), we have

$$\begin{aligned} \mathcal{P}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, t) &= \frac{1}{4\pi^2 c} \int_{-\infty}^{+\infty} d\omega e^{-i\omega t} \int_{-\infty}^{+\infty} dE \\ &\times \phi_{\alpha\beta}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_2, E + \frac{\omega}{2} + i0, \\ &E - \frac{\omega}{2} - i0). \end{aligned} \quad (14)$$

The master equation can therefore be also described using the p - h Green's function. We will refer to this equation in Sec. V.

III. GREEN'S FUNCTION EXPRESSION FOR OPTICAL SUSCEPTIBILITIES

When an external field is applied, the total Hamiltonian becomes

$$H_T(t) = H - \sum_{r\alpha} \hat{P}_{r\alpha} \cdot E_\alpha(\mathbf{r}, t). \quad (15)$$

Here $E_\alpha(\mathbf{r}, t)$ is the component of external electrical field along the α direction. $\hat{P}_{r,\alpha}$ is the α component of the dipole operator at site \mathbf{r} ,

$$\hat{P}_{r\alpha} = \mu(B_{r\alpha} + B_{r\alpha}^\dagger). \quad (16)$$

The linear polarization of the system is related to the external field through the linear response function $\chi_{\alpha\beta}^{(1)}(\mathbf{r}, t)$, i.e.,

$$\bar{P}_\alpha(\mathbf{r}, t) \equiv \sum_{r', \beta} \int_{-\infty}^t dt_1 \chi_{\alpha\beta}^{(1)}(\mathbf{r} - \mathbf{r}', t - t_1) E_\beta(\mathbf{r}', t_1). \quad (17)$$

The temporal Fourier transform of $\chi_{\alpha\beta}^{(1)}(\mathbf{r} - \mathbf{r}', t)$ can be expressed in terms of the configurationally averaged 1- p Green's function (see Appendix A)

$$\begin{aligned} \chi_{\alpha\beta}^{(1)}(\mathbf{r} - \mathbf{r}', \omega) &= \int_0^\infty dt e^{i(\omega + i0)t} \chi_{\alpha\beta}^{(1)}(\mathbf{r} - \mathbf{r}', t) \\ &= -\bar{G}_{\alpha\beta}(\mathbf{r} - \mathbf{r}', \omega + i0) \\ &\quad - \bar{G}_{\beta\alpha}(\mathbf{r}' - \mathbf{r}, -\omega - i0). \end{aligned} \quad (18)$$

Note that the configurationally averaged $\bar{G}_{\alpha,\beta}(\mathbf{r}, \mathbf{r}', z)$ depends on \mathbf{r} and \mathbf{r}' only through $\mathbf{r} - \mathbf{r}'$.

Defining the spatial Fourier transform

$$\chi_{\alpha\beta}^{(1)}(\mathbf{k}, \omega) \equiv \sum_{\mathbf{r}} e^{-i\mathbf{k} \cdot \mathbf{r}} \chi_{\alpha\beta}^{(1)}(\mathbf{r}, \omega), \quad (19)$$

$$\bar{G}_{\alpha\beta}(\mathbf{k}, z) \equiv \sum_{\mathbf{r}} e^{-i\mathbf{k} \cdot \mathbf{r}} \bar{G}_{\alpha\beta}(\mathbf{r}, z), \quad (20)$$

we have

$$\chi_{\alpha\beta}^{(1)}(\mathbf{k}, \omega) = -\bar{G}_{\alpha\beta}(\mathbf{k}, \omega + i0) - \bar{G}_{\beta\alpha}(-\mathbf{k}, -\omega - i0). \quad (21)$$

From Eqs. (7) and (21), we see that the configurationally averaged 1- p Green's function contains the necessary information for computing the density of states $N(E)$ and the linear susceptibility $\chi_{\alpha\beta}^{(1)}(\mathbf{k}, \omega)$.

Nonlinear optical techniques provide additional information not contained in the 1- p Green's function. In our model, the atom has no permanent dipole moment and $\chi^{(3)}$ is the lowest nonvanishing nonlinear susceptibility. We expand the external field in plane waves

$$E(\mathbf{r}, t) = \sum_{\alpha=1}^3 E_\alpha(\mathbf{r}, t) + \text{c.c.} \quad (22)$$

and

$$E_\alpha(\mathbf{r}, t) = E_\alpha \hat{\mu}_\alpha \exp[i(\mathbf{k}_\alpha \cdot \mathbf{r} - \omega_\alpha t)], \quad (23)$$

where $\hat{\mu}_\alpha$ is the unit polarization vector of $E_\alpha(\mathbf{r}, t)$ and c.c. denotes the complex conjugate. The third order polarization is given by

$$\begin{aligned} P_\mu^{(3)}(\mathbf{r}, t) &\equiv (-i) \sum_{\alpha, \beta, \gamma=1}^3 \sum_{\mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3} \int_0^\infty dt_1 \int_0^\infty dt_2 \\ &\quad \times \int_0^\infty dt_3 R_{\mu\alpha\mu\beta\mu\gamma}^{(3)}(\mathbf{r}t; \mathbf{r}_3 t_3, \mathbf{r}_2 t_2, \mathbf{r}_1 t_1) \\ &\quad \times E_\alpha(\mathbf{r}_3, t - t_3) E_\beta(\mathbf{r}_2, t - t_3 - t_2) \\ &\quad \times E_\gamma(\mathbf{r}_1, t - t_3 - t_2 - t_1). \end{aligned} \quad (24)$$

Here $R_{\mu\alpha\mu\beta\mu\gamma}^{(3)}(\mathbf{r}t; \mathbf{r}_3 t_3, \mathbf{r}_2 t_2, \mathbf{r}_1 t_1)$ is the third order nonlinear response function¹⁵ whose Fourier transform yields the third order nonlinear susceptibility

$$\begin{aligned} \chi_{\mu\mu_3\mu_2\mu_1}^{(3)}(-\mathbf{k}_s - \omega_s; \mathbf{k}_1 \omega_1, -\mathbf{k}_2 - \omega_2, \mathbf{k}_3 \omega_3) &= (-i) \sum_{\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3} \sum_{\text{perm}} \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 R_{\mu\mu_3\mu_2\mu_1}(\mathbf{r}t; \mathbf{r}_3 t_3, \mathbf{r}_2 t_2, \mathbf{r}_1 t_1) \\ &\quad \times \exp[i\omega_s t_3 + i(\omega_\beta + \omega_\gamma) t_2 + i\omega_\gamma t_1] \exp[i\mathbf{k}_\alpha \cdot (\mathbf{r}_3 - \mathbf{r}) + i\mathbf{k}_\beta \cdot (\mathbf{r}_2 - \mathbf{r}) + i\mathbf{k}_\gamma \cdot (\mathbf{r}_1 - \mathbf{r})]. \end{aligned} \quad (25)$$

Here

$$\mathbf{k}_s = \mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3, \quad \omega_s = \omega_1 - \omega_2 + \omega_3,$$

and Σ_{perm} denotes the sum over all permutations of the fields

$$(\mathbf{k}_\alpha \omega_\alpha, \mathbf{k}_\beta \omega_\beta, \mathbf{k}_\gamma \omega_\gamma) = (\mathbf{k}_1 \omega_1, -\mathbf{k}_2 - \omega_2, \mathbf{k}_3, \omega_3).$$

For the present model in which only the excited states are disordered, $\chi^{(3)}$ is related to the product of three Green's function. When ω_s is off resonance, we show in Appendix C that $\chi^{(3)}$ can be expressed in terms of the configurationally averaged p - h Green's function

$$\begin{aligned} \chi_{\mu\mu_3\mu_2\mu_1}^{(3)}(-\mathbf{k}_s-\omega_s, \mathbf{k}_1\omega_1, -\mathbf{k}_2-\omega_2, \mathbf{k}_3\omega_3) = & \sum_{\text{perm}} \sum_{\mathbf{r}_2, \mathbf{r}_4} \exp[i\mathbf{k}_\beta \cdot (\mathbf{r}_4 - \mathbf{r}_1) + i\mathbf{k}_\gamma \cdot (\mathbf{r}_2 - \mathbf{r}_1)] \\ & \times \left[\phi_{\mu\mu_\gamma}^{\mu\alpha\mu\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_4, \omega_\gamma + i0, -\omega_\beta - i0) / (\omega_s - \Omega) \right. \\ & + \delta_{\mu\mu_\alpha} \sum_{\sigma} \phi_{\sigma\mu_\gamma}^{\sigma\mu\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_4, \omega_\gamma + i0, -\omega_\beta - i0) / (\omega_s - \Omega) \\ & - \phi_{\mu\alpha\mu_\gamma}^{\mu\mu\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_4, \omega_\gamma + i0, -\omega_\beta - i0) / (\omega_s + \Omega) \\ & \left. - \delta_{\mu\mu_\alpha} \sum_{\sigma} \phi_{\sigma\mu_\gamma}^{\sigma\mu\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_4, \omega_\gamma + i0, -\omega_\beta - i0) / (\omega_s + \Omega) \right]. \end{aligned} \quad (26)$$

Since $\chi^{(3)}$ is defined in momentum space, we define the p - h Green's function in momentum space as the spatial Fourier transform of the p - h Green's function in coordinate space

$$\begin{aligned} \phi_{\alpha\beta}^{\sigma\gamma}(\mathbf{p}, \mathbf{p}', \mathbf{q}, z_1, z_2) \equiv & \frac{1}{M} \sum_{\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4} \phi_{\alpha\beta}^{\sigma\gamma}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, z_1, z_2) \\ & \times \exp[-i(\mathbf{p} + \mathbf{q}/2) \cdot \mathbf{r}_1 + i(\mathbf{p}' + \mathbf{q}/2) \cdot \mathbf{r}_2 \\ & + i(\mathbf{p} - \mathbf{q}/2) \cdot \mathbf{r}_3 - i(\mathbf{p}' - \mathbf{q}/2) \cdot \mathbf{r}_4], \end{aligned} \quad (27)$$

the inverse Fourier transform of which is

$$\begin{aligned} \phi_{\alpha\beta}^{\sigma\gamma}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, z_1, z_2) \equiv & \frac{1}{M^3} \sum_{\mathbf{p}, \mathbf{p}', \mathbf{q}} \phi_{\alpha\beta}^{\sigma\gamma}(\mathbf{p}, \mathbf{p}', \mathbf{q}, z_1, z_2) \exp[i\mathbf{p} \cdot (\mathbf{r}_1 \\ & - \mathbf{r}_3) + i\mathbf{p}' \cdot (\mathbf{r}_4 - \mathbf{r}_2) \end{aligned}$$

$$+ i\frac{\mathbf{q}}{2} \cdot (\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{r}_3 - \mathbf{r}_4)]. \quad (28)$$

From Eq. (26), we see that we need $\phi_{\mu\mu_\gamma}^{\mu\alpha\mu\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, z_1, z_2)$ with $\mathbf{r}_1 = \mathbf{r}_3$ only, which corresponds to summing over p in momentum space. We define a new quantity $\phi_{\alpha\beta}^{\sigma\gamma}(\mathbf{p}', \mathbf{q}, z_1, z_2)$ as

$$\begin{aligned} \phi_{\alpha\beta}^{\sigma\gamma}(\mathbf{p}', \mathbf{q}, z_1, z_2) \equiv & \frac{1}{M} \sum_{\mathbf{p}} \phi_{\alpha\beta}^{\sigma\gamma}(\mathbf{p}, \mathbf{p}', \mathbf{q}, z_1, z_2) \\ = & \sum_{\mathbf{r}_2, \mathbf{r}_4} \phi_{\alpha\beta}^{\sigma\gamma}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_4) \exp[i(\mathbf{p}' + \mathbf{q}/2) \\ & \cdot (\mathbf{r}_2 - \mathbf{r}_1)] \exp[-i(\mathbf{p}' - \mathbf{q}/2) \cdot (\mathbf{r}_4 - \mathbf{r}_1)]. \end{aligned} \quad (29)$$

We can then rewrite Eq. (26) as

$$\begin{aligned} \chi_{\mu\mu_3\mu_2\mu_1}^{(3)}(-\mathbf{k}_s-\omega_s, \mathbf{k}_1\omega_1, -\mathbf{k}_2-\omega_2, \mathbf{k}_3\omega_3) = & \frac{1}{\omega_s - \Omega} \sum_{\text{perm}} \phi_{\mu\mu_\gamma}^{\mu\alpha\mu\beta} \left(\frac{\mathbf{k}_\gamma - \mathbf{k}_\beta}{2}, \mathbf{k}_\gamma + \mathbf{k}_\beta, \omega_\gamma + i0, -\omega_\beta - i0 \right) \\ & - \frac{1}{\omega_s + \Omega} \sum_{\text{perm}} \phi_{\mu\alpha\mu_\gamma}^{\mu\mu\beta} \left(\frac{\mathbf{k}_\gamma - \mathbf{k}_\beta}{2}, \mathbf{k}_\beta + \mathbf{k}_\gamma, \omega_\gamma + i0, -\omega_\beta - i0 \right) \\ & + \frac{2\Omega}{\omega_s^2 - \Omega^2} \sum_{\text{perm}} \delta_{\mu\mu_\alpha} \sum_{\sigma} \phi_{\sigma\mu_\gamma}^{\sigma\mu\beta} \left(\frac{\mathbf{k}_\gamma - \mathbf{k}_\beta}{2}, \mathbf{k}_\gamma + \mathbf{k}_\beta, \omega_\gamma + i0, -\omega_\beta - i0 \right). \end{aligned} \quad (30)$$

This equation holds provided ω_s is off resonance. There are six permutation of $\alpha\beta\gamma$. We further assume that ω_1 and ω_2 are tuned inside the exciton band, whereas ω_3 is tuned far off resonance (see Fig. 1) and invoke the rotating wave approximation. The only resonance term in Eq. (30) is the term with $\alpha=3$, $\beta=2$, and $\gamma=1$. We thus have

$$\begin{aligned} \chi_{\mu\mu_3\mu_2\mu_1}^{(3)}(-\mathbf{k}_s-\omega_s, \mathbf{k}_1\omega_1, -\mathbf{k}_2-\omega_2, \mathbf{k}_3\omega_3) = & \frac{1}{\omega_s - \Omega} \phi_{\mu_3\mu_1}^{\mu_3\mu_2} \left(\frac{\mathbf{k}_1 + \mathbf{k}_2}{2}, \mathbf{k}_1 - \mathbf{k}_2, \omega_1 + i0, \omega_2 - i0 \right) \\ & - \frac{1}{\omega_s + \Omega} \phi_{\mu_3\mu_1}^{\mu\mu_2} \left(\frac{\mathbf{k}_1 + \mathbf{k}_2}{2}, \mathbf{k}_1 - \mathbf{k}_2, \omega_1 + i0, \omega_2 - i0 \right) \\ & + \frac{2\Omega}{\omega_s^2 - \Omega^2} \delta_{\mu\mu_3} \sum_{\sigma} \phi_{\sigma\mu_1}^{\sigma\mu_2} \left(\frac{\mathbf{k}_1 + \mathbf{k}_2}{2}, \mathbf{k}_1 - \mathbf{k}_2, \omega_1 + i0, \omega_2 - i0 \right). \end{aligned} \quad (31)$$

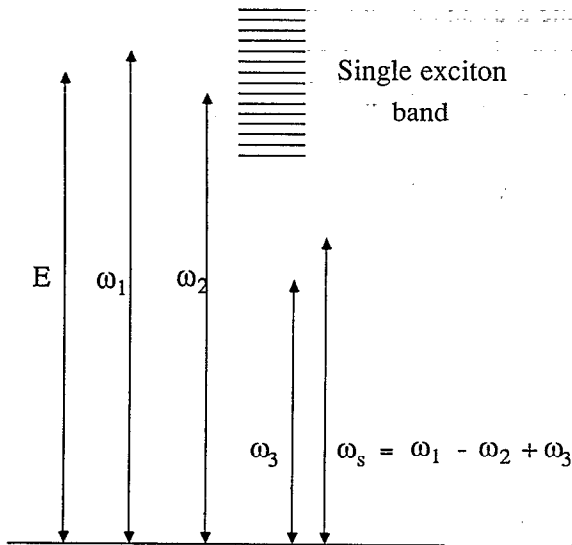


FIG. 1. A schematic representation of the degenerate four wave mixing experiment. The ω_1, ω_2 frequencies are tuned within the exciton band and form a grating, which is probed by the off resonance beam ω_3 , generating a signal with frequency $\omega_s = \omega_1 - \omega_2 + \omega_3$ (direction $k_s = k_1 - k_2 + k_3$). An extra resonance observed when $\omega_1 = \omega_2$ provides a direct probe for exciton transport. $E = (\omega_1 + \omega_2)/2$.

In Sec. V, we shall calculate this p - h Green's function and predict the appearance of an extra resonance which provide a direct probe for exciton transport.

IV. 1- P GREEN'S FUNCTION AND THE LINEAR OPTICAL SUSCEPTIBILITY

In this section, we evaluate the 1- p Green's function using the coherent potential approximation (CPA).¹ The details are given in Appendix D. In the CPA the configurationally averaged 1- p Green's function in momentum space is

$$\bar{G}_{\mu\nu}(\mathbf{k}, z) = G_{\mu\nu}^{\text{eff}}(\mathbf{k}, z) = \{ [z - \Omega - \Sigma(z)] \cdot \mathbf{1} - J(\mathbf{k}) \}_{\mu\nu}^{-1}. \quad (32)$$

Here $\mathbf{1}$ is unit 3 by 3 matrix, $J(\mathbf{k})$ is also a 3 by 3 matrix whose $\alpha\beta$ matrix element is $J_{\alpha\beta}(\mathbf{k})$, the spatial Fourier transform of dipole-dipole interaction tensor

$$J_{\alpha\beta}(\mathbf{k}) = \sum_{\mathbf{r} \neq 0} J_{\alpha\beta}(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}}. \quad (33)$$

The self-energy $\Sigma(z)$ is determined by the self-consistent equation

$$(1-c) \cdot \frac{\epsilon_1 - \Omega - \Sigma(z)}{1 - [\epsilon_1 - \Omega - \Sigma(z)] G_{\mu\mu}^{\text{eff}}(r, r, z)} - \frac{c\Sigma(z)}{1 + \Sigma(z) G_{\mu\mu}^{\text{eff}}(r, r, z)} = 0 \quad (34)$$

As indicated in Sec. II, the topologically disordered model can be obtained from this result by taking the $\epsilon_1 \rightarrow \infty$ limit, we thus have

$$\Sigma(z) \int d\epsilon \frac{N^0(\epsilon)}{z - \Sigma(z) - \epsilon} = c - 1. \quad (35)$$

We have used Eq. (D12). Here $N^0(\epsilon)$ is the density of states of the regular lattice ($c=1$), on which the atoms are distributed,

$$\begin{aligned} N^0(\epsilon) &= \frac{1}{3M} \text{Tr}[\delta(\epsilon - \hat{H}^0)] \\ &= \frac{1}{3\Omega_{\text{1.B.Z.}}} \sum_{a=1}^3 \int_{\text{1.B.Z.}} d^3k \delta[\epsilon - \Omega - J_a(\mathbf{k})], \end{aligned} \quad (36)$$

and \hat{H}^0 is the regular lattice Hamiltonian ($c=1$)

$$\hat{H}^0 = \sum_{\mathbf{r}, \alpha} \Omega B_{\mathbf{r}\alpha}^+ B_{\mathbf{r}\alpha} + \sum_{\mathbf{r} \neq \mathbf{r}', \alpha, \beta} J_{\alpha\beta}(\mathbf{r} - \mathbf{r}') B_{\mathbf{r}\alpha}^+ B_{\mathbf{r}'\beta}. \quad (37)$$

In Eq. (36), $\Omega_{\text{1.B.Z.}}$ is the volume of first Brillouin zone and $J_a(\mathbf{k})$, $a=1, 2, 3$ are the eigenvalues of the matrix $J(\mathbf{k})$. The procedure for calculating $J(\mathbf{k})$ is given in Appendix E. By diagonalizing this matrix, we find the density of states of the regular lattice $N^0(E)$. This is the only input to the self-consistent equation (35). We have solved the equation numerically for $\Sigma(z)$ by finding the complex root for a given complex number z , using Newton's method.¹⁶ Substituting $\Sigma(z)$ into Eq. (32), we obtain the 1- p Green's function.

Substituting Eq. (32) into Eq. (21) and using the rotating wave approximation, we get the linear susceptibility

$$\chi_{\alpha\beta}^{(1)}(\mathbf{k}, \omega) = - \{ [\omega - \Omega - \Sigma(\omega + i0)] \cdot \mathbf{1} - J(\mathbf{k}) \}_{\alpha\beta}^{-1}. \quad (38)$$

The behavior of $J(\mathbf{k})$ near $\mathbf{k}=0$ is pathological and needs to be treated very carefully.^{17,18} Typically in macroscopic experiment, the wavelength of light is much greater than the lattice constant a , but also much smaller than the sample size R , i.e.,

$$ka \ll 1 \ll kR, \quad (39)$$

where k is the optical wave vector of the applied field. We have¹⁷

$$J_{\alpha\beta}(\mathbf{k}) = -\frac{4\pi}{3} J_0 (\delta_{\alpha\beta} - 3\hat{k}_\alpha \hat{k}_\beta). \quad (40)$$

Here $J_0 \equiv |\mu|^2/v$, v is the volume of a unit cell and $\hat{\mathbf{k}} = \mathbf{k}/k$. Substituting Eq. (40) into Eq. (38), we have

$$\begin{aligned} \epsilon_{\mu\nu}(\mathbf{k}, \omega) &\equiv \delta_{\mu\nu} + 4\pi J_0 \chi_{\mu\nu}^{(1)}(\mathbf{k}, \omega) \\ &= \delta_{\mu\nu} - \frac{4\pi J_0}{\omega - \Omega - \Sigma(\omega + i0) + 4\pi J_0/3} \\ &\quad \times \left[\delta_{\mu\nu} + \frac{4\pi J_0}{\omega - \Omega - \Sigma(\omega + i0) - 8\pi J_0/3} \hat{k}_\mu \hat{k}_\nu \right]. \end{aligned} \quad (41)$$

As the external field is transverse ($\mathbf{E} \cdot \mathbf{k} = 0$), we are only interested in the isotropic part of ϵ ,

$$\epsilon_{\mu\nu}(\mathbf{k}, \omega) = \epsilon(\omega) \delta_{\mu\nu}, \quad (42a)$$

$$\epsilon(\omega) = 1 - \frac{4\pi J_0/3}{\omega - \Omega - \Sigma(\omega + i0) + 4\pi J_0/3}. \quad (42b)$$

The above expression gives the dielectric function $\epsilon(\omega)$ for a crystal whose physical size R is much greater than the optical wavelength.

We next consider the linear polarizability $\alpha_{\mu\nu}(\omega)$ of an aggregate whose size is much smaller than the optical wavelength, i.e., $kR \ll 1$, we have¹⁷ $J_{\mu\nu}(\mathbf{k}) = 0$. Therefore

$$\alpha_{\mu\nu}(\omega) = \alpha(\omega) \delta_{\mu\nu} = - \frac{|\mu|^2}{\omega - \Omega - \Sigma(\omega + i0)} \delta_{\mu\nu}. \quad (43)$$

Combining Eqs. (42) and (43), we have

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = \frac{4\pi\alpha(\omega)}{3v}. \quad (44)$$

This is similar to the Clausius Mossotti relation, except that $\alpha(\omega)$ is the polarizability of a small cluster rather than a single atom. When $c \rightarrow 0$, Eq. (35) shows

$$\Sigma = -(\omega - \Omega)/c.$$

Substituting this into Eq. (43) and then substituting into Eq. (44), we obtain the standard Clausius Mossotti relation

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = \frac{4\pi\rho\alpha_0(\omega)}{3}, \quad (45)$$

where $\rho = c/v$ is the density of atoms and $\alpha_0(\omega) = -|\mu|^2/(\omega - \Omega)$ is the polarizability of single atom.

We have calculated the density of states $N(E)$ and the absorption line shape $A(\omega) = \text{Im} \chi^{(1)}(k \rightarrow 0, \omega + i0)$ of a face-centered-cubic (fcc) lattice with dipole-dipole interactions. The results are presented in Figs. 2 and 3(B). From Fig. 2, we see that the absorption peak is at the bottom of the band. As c decreases, the absorption peak shifts to higher energy and the width increases, while the maximum absorption decreases. However, for low density, the absorption linewidth decreases again (not shown in figures) because the band narrows. Therefore, the absorption linewidth attains a maximum value at some intermediate density. Huber and Ching¹⁹ calculated the absorption line shape of a simple cubic lattice of binary alloy of two level atoms with nearest neighbor interaction. They found the width predicted by the simple CPA to be smaller than simulation results. The simple CPA takes into account the scattering from a single site and therefore underestimates the effect of multiple scattering sequences. The CPA may be improved systematically by using the cluster CPA,²⁰ which exactly takes into account the scattering within a small cluster.

V. LADDER DIAGRAM APPROXIMATION FOR THE P - H GREEN'S FUNCTION

In Sec. III, we derived a formal expression of $\chi^{(3)}$ of D4WM in terms of the configurationally averaged p - h Green's functions [see Eq. (31)]. In this section, we will

evaluate it using the ladder diagram approximation. A detailed description of the ladder diagram approximation is given in Ref. 8. We start with the Bethe-Salpeter equation^{6,8} for the configurationally averaged p - h Green's function

$$\begin{aligned} \phi_{\alpha\beta}^{\sigma\gamma}(\mathbf{p}, \mathbf{p}', \mathbf{q}, z_1, z_2) &= M \bar{G}_{\alpha\beta}(\mathbf{p} + \mathbf{q}/2, z_1) \bar{G}_{\gamma\sigma}(\mathbf{p} - \mathbf{q}/2, z_2) \delta_{\mathbf{p}, \mathbf{p}'} \\ &+ \frac{1}{M} \sum_{\alpha', \beta', \sigma', \gamma', \mathbf{p}''} \bar{G}_{\alpha\alpha'}(\mathbf{p} \\ &+ \mathbf{q}/2, z_1) \bar{G}_{\sigma'\sigma}(\mathbf{p} - \mathbf{q}/2, z_2) \\ &\times \Gamma_{\alpha'\beta'}^{\sigma'\gamma'}(\mathbf{p}, \mathbf{p}'', \mathbf{q}, z_1, z_2) \phi_{\beta'\beta}^{\gamma'\gamma}(\mathbf{p}'', \mathbf{p}', \mathbf{q}, z_1, z_2). \end{aligned} \quad (46)$$

Here Γ may be calculated using a summation of all the irreducible diagrams. The ladder diagram approximation⁸ keeps only those diagrams without crossing (single site diagrams) in Γ , i.e., it assumes

$$\Gamma_{\alpha'\beta'}^{\sigma'\gamma'}(\mathbf{p}, \mathbf{p}'', \mathbf{q}, z_1, z_2) = A_{\alpha'\beta'}^{\sigma'\gamma'}(z_1, z_2), \quad (47)$$

where $A_{\alpha'\beta'}^{\sigma'\gamma'}(z_1, z_2)$ denotes the summation of all the single site diagrams. Another way of formulating the approximation is by postulating that Γ does not depend on \mathbf{p} , \mathbf{p}' , \mathbf{q} . In r space, Γ is assumed to be a delta function hence the name single site approximation. The physical significance of the ladder diagram approximation is that it assumes that the bra and ket of the density matrix are scattered by the same sequence of impurities during the propagation and all scattering processes are independent. Suppose the bra and ket of the density matrix are scattered by sites $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n$, the scattering strength is proportional to $t_{r_1}^2 t_{r_2}^2 \dots t_{r_n}^2$, where t_r is the scattering t matrix of a single site r . Since we assume the scattering processes to be independent, we have

$$\overline{t_{r_1}^2 t_{r_2}^2 \dots t_{r_n}^2} = A^n. \quad (48)$$

Here A is the renormalized single site scattering strength $\overline{t_r^2}$ to be determined self-consistently. In our model, each site has three possible excited states, so A is a fourth rank tensor $A_{\alpha'\beta'}^{\sigma'\gamma'}(z_1, z_2)$ with 81 components. For a simple cubic fcc or bcc lattice, the fourth rank tensor A which has cubic symmetry, i.e., x , y , and z axes are equivalent and the tensor is invariant for the inversion of any axis. In Appendix B, we show that the only nonzero components of the fourth rank tensor A are

$$A_{\alpha\alpha'}^{\beta\beta} A_{\alpha\beta}^{\alpha\beta} A_{\alpha\beta}^{\beta\alpha} \quad \alpha, \beta = P_x P_y P_z.$$

We will later derive a self-consistent equation to determine these components.

Considering the special case $\mu_1 = \mu_2$, i.e., the external fields $\mathbf{E}_1 \parallel \mathbf{E}_2$, we show from Appendix F that when $\mathbf{q} = |\mathbf{k}_1 - \mathbf{k}_2|$ is along one of the principle axes (x , y , or z axis) of the cubic lattice,

$$\phi_{\mu\mu_1}^{\mu_3\mu_1}[(\mathbf{k}_1 + \mathbf{k}_2)/2, \mathbf{k}_1 - \mathbf{k}_2, z_1, z_2]$$

is nonzero only if $\mu = \mu_3$. From Eq. (31), we have

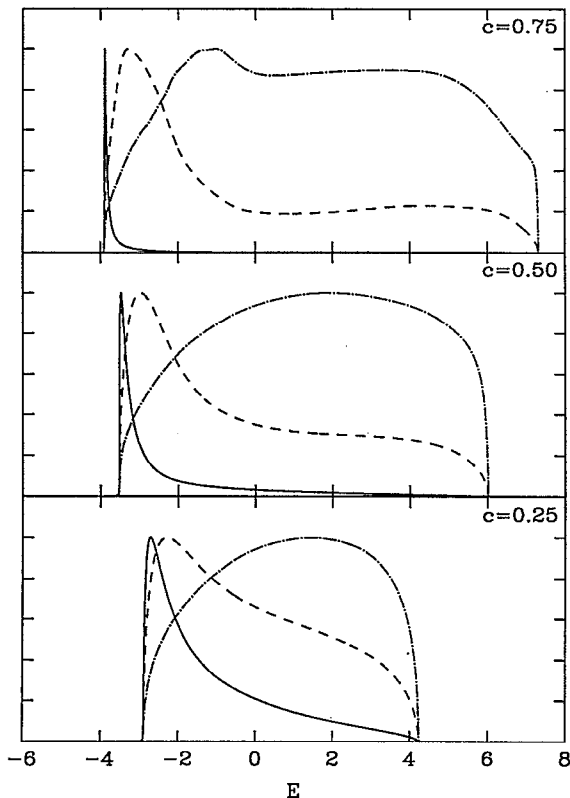


FIG. 2. Linear absorption line shape $A(E)$ (solid line), density of states $N(E)$ (dashed line), and diffusion coefficient $D(E)$ (dashed dotted line) as a function of energy E at three different densities. All curves are normalized to the same height. The relative value of the maximum absorption are 41.5 : 6.1 : 1 for $c=0.75, 0.50,$ and 0.25 . $\mu=1, \nu=1$, where μ is defined in Eq. (5) and ν is the volume of the unit cell of the lattice. The energy E is given in unit of μ^2/ν .

$$\begin{aligned} &\chi_{\mu_3\mu_1\mu_1}(-\mathbf{k}_s-\omega_s, \mathbf{k}_1\omega_1, -\mathbf{k}_2-\omega_2, \mathbf{k}_3\omega_3) \\ &= \frac{2\Omega}{\omega_s^2 - \Omega^2} \delta_{\mu\mu_3} \\ &\times \left\{ \phi_{\mu_3\mu_1}^{\mu_3\mu_1}[(\mathbf{k}_1+\mathbf{k}_2)/2, \mathbf{k}_1-\mathbf{k}_2, \omega_1+i0, \omega_2-i0] \right. \\ &\left. + \sum_{\sigma} \phi_{\sigma\mu_1}^{\sigma\mu_1}[(\mathbf{k}_1+\mathbf{k}_2)/2, \mathbf{k}_1-\mathbf{k}_2, \omega_1+i0, \omega_2-i0] \right\}. \end{aligned} \tag{49}$$

We define the fourth rank tensor $L_{\alpha\beta}^{\sigma\gamma}(\mathbf{q}, z_1, z_2)$ as the direct product of two configurationally averaged 1- p Green's functions

$$\begin{aligned} L_{\alpha\beta}^{\sigma\gamma}(\mathbf{q}, z_1, z_2) &\equiv \sum_{\mathbf{r}} \bar{G}_{\alpha\beta}(\mathbf{r}, z_1) \bar{G}_{\gamma\sigma}(\mathbf{r}, z_2) e^{-i\mathbf{q}\cdot\mathbf{r}} \\ &= \frac{1}{M} \sum_{\mathbf{p}} \bar{G}_{\alpha\beta}(\mathbf{p}+\mathbf{q}/2, z_1) \bar{G}_{\gamma\sigma}(\mathbf{p}-\mathbf{q}/2, z_2). \end{aligned} \tag{50}$$

In Appendix F, we derive the relation between L and ϕ ,

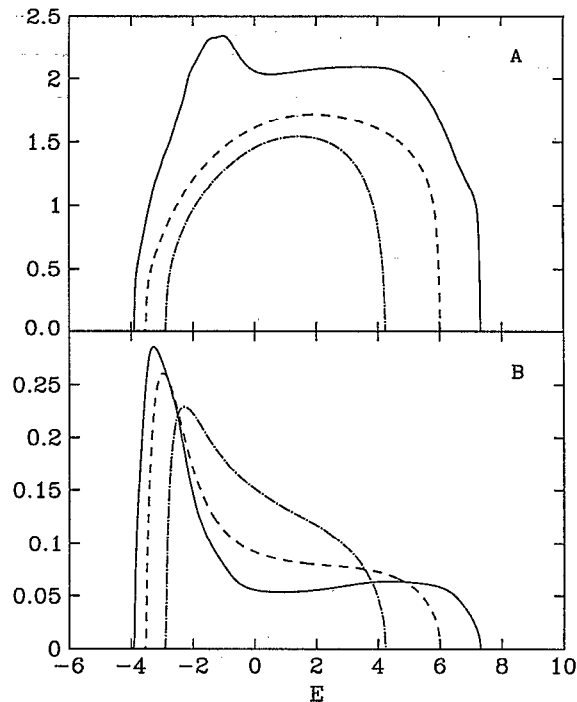


FIG. 3. (A) diffusion coefficient $D(E)$ as a function of energy at three different densities $c=0.75$ (solid line), $c=0.50$ (dashed line), and $c=0.25$ (dashed-dotted line). $\mu=1, \nu=1$, where μ is defined in Eq. (5) and ν is the volume of the unit cell of the lattice. The energy E is given in unit of μ^2/ν . (B) Density of states $N(E)$ as a function of energy at three different densities as in (A).

$$\begin{aligned} &\phi_{\mu_3\mu_1}^{\mu_3\mu_1}[(\mathbf{k}_1+\mathbf{k}_2)/2, \mathbf{k}_1-\mathbf{k}_2, z_1, z_2] \\ &= [1 - L(\mathbf{k}_1-\mathbf{k}_2, z_1, z_2) \\ &\cdot A(z_1, z_2)]_{\mu_3\mu_1}^{-1} \bar{G}_{\mu_1\mu_1}(\mathbf{k}_1, z_1) \bar{G}_{\mu_1\mu_1}(\mathbf{k}_2, z_2) \end{aligned} \tag{51}$$

with $\mu_3 = p_x p_y p_z$

Here L and A are 3 by 3 matrices whose $\alpha\beta$ matrix elements are $L_{\alpha\beta}^{\alpha\beta}$ and $A_{\alpha\beta}^{\alpha\beta}$. Note that these matrices are specific components of the corresponding fourth rank tensor, they are not second rank tensors, and the symmetry argument of Appendix B does not apply to them. The matrix $A(z_1, z_2)$ will be determined by the self-consistent equation (see Appendix F)

$$\begin{aligned} &\sum_{\beta} \{ [1 - L(\mathbf{q}=\mathbf{0}, z_1, z_2) \cdot A(z_1, z_2)]^{-1} \cdot L(\mathbf{q}=\mathbf{0}, z_1, z_2) \}_{\alpha\beta} \\ &= \frac{\bar{G}_{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_1, z_2) - \bar{G}_{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_1, z_1)}{z_1 - z_2}, \end{aligned} \tag{52}$$

which is related to the conservation of the number of excitons. We can solve the matrix $A(z_1, z_2)$ from Eq. (52) and then substitute into Eq. (51) to determine $\phi_{\mu_3\mu_1}^{\mu_3\mu_1}$. If the lattice is simple cubic, fcc or bcc, the x, y, z direction are equivalent. The matrix $A_{\alpha\beta}^{\alpha\beta}$ has only two independent components—the diagonal element $A_1(z_1, z_2)$ and the off diagonal element $A_2(z_1, z_2)$. We can write $A_{\alpha\beta}^{\alpha\beta}$ as

$$A_{\alpha\beta}^{\alpha\beta}(z_1, z_2) = A_1(z_1, z_2) \delta_{\alpha\beta} + A_2(z_1, z_2) (1 - \delta_{\alpha\beta}). \tag{53}$$

Since we have only one equation for A matrix [Eq. (52)], we take A_2 as a parameter, solve A_1 in terms of A_2 by Eq. (52), and then substitute it into Eq. (51) to calculate $\phi_{\mu_3\mu_1}^{\mu_3\mu_1}$. The result is expected to depend on the parameter $A_2(z)$. Define

$$\omega_1 \equiv E + \omega_{12}/2, \quad \omega_2 \equiv E - \omega_{12}/2. \quad (54)$$

We take E to be inside the exciton band, $\omega_{12} = \omega_1 - \omega_2$ is very small, and $q = |\mathbf{k}_1 - \mathbf{k}_2|$ is also very small (see Fig. 1). In the hydrodynamic limit ($q \rightarrow 0$, $\omega_{12} \rightarrow 0$), we expand the solution

$$\phi_{\mu_3\mu_1}^{\mu_3\mu_1}((\mathbf{k}_1 + \mathbf{k}_2)/2, \mathbf{k}_1 - \mathbf{k}_2, \omega_1 + i0, \omega_2 - i0)$$

and keep only the lowest nonzero terms in q and ω_{12} . The result is

$$\phi_{\mu_3\mu_1}^{\mu_3\mu_1}((\mathbf{k}_1 + \mathbf{k}_2)/2, \mathbf{k}_1 - \mathbf{k}_2, \omega_1 + i0, \omega_2 - i0) = \frac{2\pi icN(E) \bar{G}_{\mu_1\mu_1}(\mathbf{k}_1, \omega_1 + i0) \bar{G}_{\mu_1\mu_1}(\mathbf{k}_2, \omega_2 - i0)}{[\omega_{12} + i|\mathbf{k}_1 - \mathbf{k}_2|^2 D(E)] L_0(E)}, \quad (55)$$

where

$$D(E) = 6\pi cN(E) L_2(E) / [L_0(E)]^2, \quad (56)$$

$L_0(E)$ and $L_2(E)$ are defined as

$$\begin{aligned} L_0(E) &= \sum_{\mathbf{r}, \alpha, \beta} |\bar{G}_{\alpha\beta}(\mathbf{r}, E + i0)|^2 \\ &= \frac{1}{M} \sum_{\mathbf{p}, \alpha, \beta} |\bar{G}_{\alpha\beta}(\mathbf{p}, E + i0)|^2, \\ L_2(E) &= \frac{1}{2} \sum_{\mathbf{r}, \alpha, \beta} |\bar{G}_{\alpha\beta}(\mathbf{r}, E + i0)|^2 x^2 \\ &= \frac{1}{2M} \sum_{\mathbf{p}, \alpha, \beta} |\partial \bar{G}_{\alpha\beta}(\mathbf{p}, E + i0) / \partial p_x|^2. \end{aligned} \quad (57) \quad (58)$$

Note that in the small q limit, we can perform a Taylor expansion on Eq. (50)

$$\sum_{\alpha\beta} L_{\alpha\beta}^{\alpha\beta}(q, E + i0, E - i0) = L_0(E) - q^2 L_2(E) + O(q^4).$$

We now make a connection to exciton transport. From Eq. (14), we see that the exciton transport is related to p - h Green's function with $\mathbf{r}_1 = \mathbf{r}_3$, $\mathbf{r}_2 = \mathbf{r}_4$ which is equivalent to the summation of p and p' in momentum space. We then define

$$\begin{aligned} \phi_{\alpha\beta}^{\alpha\beta}(\mathbf{q}, z_1, z_2) &\equiv \frac{1}{M^2} \sum_{\mathbf{p}, \mathbf{p}'} \phi_{\alpha\beta}^{\alpha\beta}(\mathbf{p}, \mathbf{p}', \mathbf{q}, z_1, z_2) \\ &= \frac{1}{M} \sum_{\mathbf{r}_1, \mathbf{r}_2} \phi_{\alpha\beta}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_2) \exp[-i\mathbf{q} \cdot (\mathbf{r}_1 - \mathbf{r}_2)]. \end{aligned} \quad (59)$$

From Appendix F, we have

$$\phi_{\alpha\beta}^{\alpha\beta}(\mathbf{q}, z_1, z_2) = \sum_{\beta'} [\mathbf{1} - L(\mathbf{q}, z_1, z_2) \cdot A(z_1, z_2)]_{\alpha\beta}^{-1} \cdot L_{\beta'\beta}(\mathbf{q}, z_1, z_2). \quad (60)$$

In the hydrodynamic limit ($q \rightarrow 0$, $\omega \rightarrow 0$), we have

$$\phi_{\alpha\beta}^{\alpha\beta}\left(\mathbf{q}, E + \frac{\omega}{2} + i0, E - \frac{\omega}{2} - i0\right) = \frac{2\pi icN(E)}{3[\omega + iq^2 D(E)]}. \quad (61)$$

We thus identify $D(E)$ [defined in Eq. (56)] as the exciton diffusion coefficient^{7,8} at energy E . Note that the right-hand side of the above equation does not depend on α and β , which means that the diffusion coefficient does not depend on the initial and final polarizations of the exciton. The physical interpretation is that in the hydrodynamic (large distance and long time) limit, due to the randomness of the system, the exciton loses memory of its initial polarization and becomes depolarized. Consequently, $\phi_{\mu_3\mu_1}^{\mu_3\mu_1}$ does not depend on μ_3 , μ_1 [see Eq. (55)]. Note that $\bar{G}_{\mu_1\mu_1}(\mathbf{k}_1, \omega_1 + i0)$, $\bar{G}_{\mu_1\mu_1}(\mathbf{k}_2, \omega_2 - i0)$ does not depend on μ_1 . An interesting and useful feature of Eqs. (55) and (61) is that they do not depend on the parameter $A_2(z_1, z_2)$, so that in the hydrodynamic limit, we do not have an undetermined quantity.

From Eqs. (49) and (55), we have

$$\begin{aligned} \chi_{\mu_3\mu_1\mu_1}^{(3)}(-\mathbf{k}_s - \omega_s, \mathbf{k}_1\omega_1, -\mathbf{k}_2 - \omega_2, \mathbf{k}_3\omega_3) \\ = \frac{16\pi ic\Omega N(E) \bar{G}_{\mu_1\mu_1}(\mathbf{k}_1, \omega_1 + i0) \bar{G}_{\mu_1\mu_1}(\mathbf{k}_2, \omega_2 - i0)}{(\omega_s^2 - \Omega^2) [\omega_{12} + i|\mathbf{k}_1 - \mathbf{k}_2|^2 D(E)] L_0(E)} \delta_{\mu_3\mu_1}. \end{aligned} \quad (62)$$

The result holds only when $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$, and $\hat{\mu}_3$ and $\hat{\mu}_1$ are along the principle axis (x , y , or z axis of the cubic lattice). Under this condition, $\chi_{\mu_3\mu_1\mu_1}^{(3)}(-\mathbf{k}_s - \omega_s, \mathbf{k}_1\omega_1, -\mathbf{k}_2 - \omega_2, \mathbf{k}_3\omega_3)$ does not depend on \mathbf{q} , $\hat{\mu}_3$, and $\hat{\mu}_1$. With the slowly varying amplitude approximation, the signal intensity $S(\mathbf{k}_s, \omega_s)$ is proportional to the absolute square of $\chi^{(3)}$,

$$S(\mathbf{k}_s, \omega_s) \propto |\chi^{(3)}|^2 = \frac{W(E) |\mathbf{k}_1 - \mathbf{k}_2|^4 D^2(E)}{\omega_{12}^2 + |\mathbf{k}_1 - \mathbf{k}_2|^4 D^2(E)}. \quad (63)$$

It has a Lorentzian type resonance at $\omega_1 = \omega_2$ whose width is $|\mathbf{k}_1 - \mathbf{k}_2|^2 D(E)$. The peak of the signal $W(E)$ is

$$\begin{aligned} W(E) &= \frac{64\Omega^2}{9(\omega_s^2 - \Omega^2)^2 |\mathbf{k}_1 - \mathbf{k}_2|^4} [L_0(E)/L_2(E)]^2 \\ &\quad \times |G_{\mu_1\mu_1}(\mathbf{k}_1, \omega_1 + i0)|^2 |G_{\mu_1\mu_1}(\mathbf{k}_2, \omega_2 - i0)|^2. \end{aligned} \quad (64)$$

We have calculated the exciton diffusion coefficient $D(E)$ in a fcc lattice for different values of density c . The results are shown in Fig. 2 (dashed dotted line) and Fig. 3(A). From Fig. 3(A), we see that $D(E)$ increases with c . This is reasonable because the exciton diffuses more rapidly if there are more atoms on the lattice. We also see that the midband states are more diffusive than the band edge states. This is natural if one realizes that in this region, the exciton group velocity usually reaches its maximum. We have also calculated the peak of the signal $W(E)$ as a function of $E = (\omega_1 + \omega_2)/2$ (Fig. 4, solid line). This is analogous to the Raman excitation profile.²¹ We see that its

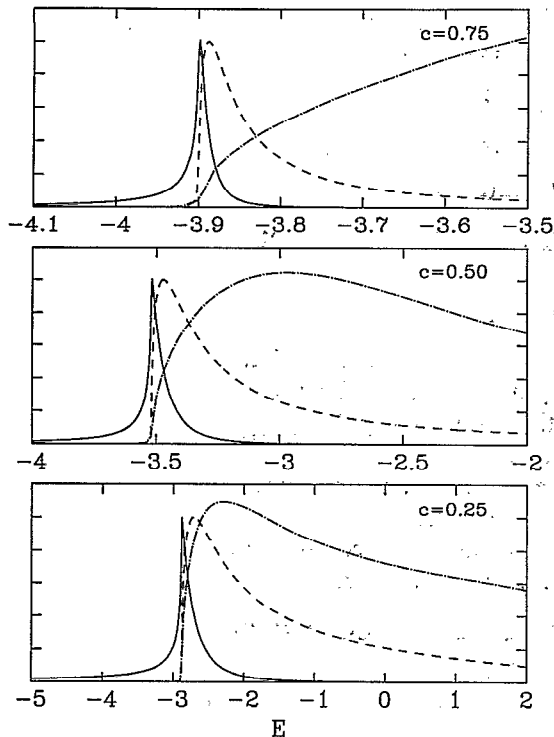


FIG. 4. The peak of the D4WM signal $W(E)$ (solid line), linear absorption line shape $A(E)$ (dashed line), and density of states $N(E)$ (dashed-dotted line) as a function of energy E at three different densities c . All curves are normalized to the same height. The relative value of the maximum $W(E)$ are 8293:85:1 for $c=0.75, 0.50$, and 0.25 . The relative values of maximum absorption are the same as in Fig. 2. $\mu=1$, $\nu=1$ where μ is defined in Eq. (5) and ν is the volume of the unit cell. The energy E is given in units of μ^2/ν .

maximum is at the bottom of the band which is slightly red shifted with respect to the maximum absorption line shape, but $W(E)$ is considerably sharper than the linear absorption line shape $A(E)$. As c is decreased, the maximum of $W(E)$ shifts to higher energy just like the linear absorption line shape, and its absolute value decreases much more rapidly than the linear absorption. This is because $W(E) \sim |\chi^{(1)}|^4$, while linear absorption $\sim \text{Im}(\chi^{(1)})$. Note that the energy scale in Fig. 4 is different for different values of density c .

VI. DISCUSSION AND CONCLUSIONS

We now examine $\chi^{(3)}$ in the regular lattice limit ($c=1$) and the isolated atom limit $c \rightarrow 0$. In the regular lattice limit, i.e., $c=1$, we have $A_{\alpha\beta}^{\gamma\delta}(z_1, z_2) = 0$. From Eq. (51), together with Eq. (49), we have

$$\begin{aligned} \chi_{\mu_3\mu_2\mu_1\mu_1}^{(3)}(-\mathbf{k}_s - \omega_s, \mathbf{k}_1\omega_1, -\mathbf{k}_2 - \omega_2, \mathbf{k}_3\omega_3) \\ = \frac{2\Omega}{\omega_s^2 - \Omega^2} \bar{G}_{\mu_1\mu_1}(\mathbf{k}_1, \omega_1 + i0) \bar{G}_{\mu_1\mu_1}(\mathbf{k}_2, \omega_2 - i0) (\delta_{\mu_3\mu_1} + 1) \\ = \frac{2\Omega}{\omega_s^2 - \Omega^2} \frac{1}{\omega_1 - \Omega + 4\pi/3\nu} \frac{1}{\omega_2 - \Omega + 4\pi/3\nu} (\delta_{\mu_3\mu_1} + 1). \end{aligned} \quad (65)$$

In the isolated atom limit, i.e., $c \rightarrow 0$, we have

$$\begin{aligned} \phi_{\mu_3\mu_1}^{\mu_2\mu_1}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_4, \omega_1 + i0, \omega_2 - i0) \\ = c \cdot \frac{1}{(\omega_1 - \Omega)(\omega_2 - \Omega)} \delta_{\mu_3\mu_1} \delta_{\mathbf{r}_1, \mathbf{r}_2} \delta_{\mathbf{r}_1, \mathbf{r}_4}. \end{aligned} \quad (66)$$

Substituting into Eq. (49), we have

$$\begin{aligned} \chi_{\mu_3\mu_2\mu_1\mu_1}^{(3)}(-\mathbf{k}_s - \omega_s, \mathbf{k}_1\omega_1, -\mathbf{k}_2 - \omega_2, \mathbf{k}_3\omega_3) \\ = c\alpha_{\mu_3\mu_1}^{(3)}(-\omega_s, \omega_1, -\omega_2, \omega_3), \end{aligned} \quad (67)$$

where $\alpha^{(3)}$ is the third order polarizability of the isolated atom

$$\begin{aligned} \alpha_{\mu_3\mu_1}^{(3)}(-\omega_s, \omega_1, -\omega_2, \omega_3) = \frac{2\Omega}{\omega_s^2 - \Omega^2} \frac{1}{(\omega_1 - \Omega)(\omega_2 - \Omega)} \\ \times (\delta_{\mu_3\mu_1} + 1). \end{aligned} \quad (68)$$

Equations (65) and (67) show that $\chi_{\mu_3\mu_2\mu_1\mu_1}^{(3)}(-\mathbf{k}_s - \omega_s, \mathbf{k}_1\omega_1, -\mathbf{k}_2 - \omega_2, \mathbf{k}_3\omega_3)$ depends on $\mu_3\mu_1$, while Eq. (62) predicts no such dependence. This discrepancy results from the fact that Eq. (62) is based on the hydrodynamic (diffusion) limit. For a regular lattice, excitons undergo coherent motion rather than diffusion, while in the low density isolated atom limit, the exciton is localized rather than diffusive. Since the diffusion is due to the random distribution of atoms, the exciton will be diffusive only beyond some cross-over distance r_c and time t_c ,²² which allows it to sample a sufficient number of atoms and holes. For any $0 < c < 1$, there is some crossover $q_c = 1/r_c$, $\omega_c = 1/t_c$; when $|\mathbf{k}_1 - \mathbf{k}_2| < q_c$, $\omega_{12} < \omega_c$, Eq. (62) is valid. At high density, there are only a small number of holes, while in small density, there are only a small number of atoms. Therefore r_c , t_c increase in both the high density and low density limits because the exciton has to travel a longer time and larger distance to sample the randomness. Consequently, q_c , $\omega_c \rightarrow 0$ in both limits. However, we can always control the external fields to make $q = |\mathbf{k}_1 - \mathbf{k}_2|$ and $\omega_{12} = \omega_1 - \omega_2$ below q_c and ω_c respectively, to make Eq. (62) valid.

Equation (62) shows that the signal of D4WM has a resonance at $\omega_1 = \omega_2$, while there is no such resonance in Eqs. (65) and (67). This is therefore a disorder induced resonance. It is analogous to the dephasing induced resonance.²³ The experiment can also be performed in the time domain result in the transient grating configuration.^{10,24}

In this paper, we calculated the third order nonlinear susceptibility of D4WM for a lattice with randomly distributed polarizable atoms. In general, $\chi^{(3)}$ is related to the configurationally averaged product of three Green's functions. We showed that $\chi^{(3)}$ of D4WM is determined only by the p - h Green's function if the frequency of the outgoing signal is far off resonance. Then we used the ladder diagram approximation to evaluate this p - h Green's function. In the hydrodynamic (small q , ω) limit, the signal intensity is shown to have a disorder induced resonance at $\omega_1 = \omega_2$ [see Eq. (62)] whose width is proportional to the exciton diffusion coefficient. We also calculated the diffusion coefficient and the peak of the D4WM signal as a

function of $E = (\omega_1 + \omega_2)/2$. In the numerical calculations, we used the simple CPA for the 1- p Green's function. However, Eq. (62) does not depend on this approximation. We can use other methods to calculate the 1- p Green's function and then substitute into Eq. (62) to calculate $\chi^{(3)}$.

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APPENDIX A: DERIVATION OF EQ. (18)

The polarization of the system is

$$P_\alpha(\mathbf{r}, t) = \text{Tr}[\hat{P}_\alpha(\mathbf{r})\rho(t)]. \quad (\text{A1})$$

Here $\rho(t)$ is the density operator at time t . According to linear response theory, the density operator evolves as

$$\rho(t) = e^{-iLt} \left[1 - i \int_{-\infty}^t dt_1 e^{iLt_1} L'(t_1) \right] \rho(-\infty), \quad (\text{A2})$$

where L and $L'(t)$ are Liouville operators. For any operator A ,

$$LA \equiv [H, A], \quad (\text{A3a})$$

$$e^{-iLt} A \equiv e^{-iHt} A e^{iHt}, \quad (\text{A3b})$$

$$L'(t) \equiv - \sum_{\mathbf{r}, \alpha} \tilde{P}_{\mathbf{r}, \alpha} E_\alpha(\mathbf{r}, t), \quad (\text{A3c})$$

$$\tilde{P}_{\mathbf{r}, \alpha} A \equiv [\tilde{P}_{\mathbf{r}, \alpha}, A]. \quad (\text{A3d})$$

Substituting Eq. (A2) into Eq. (A1) and comparing with Eq. (17), we have

$$\chi_{\alpha\beta}^{(1)}(\mathbf{r} - \mathbf{r}', t) = i \text{Tr}[\overline{P_{\mathbf{r}, \alpha} e^{-iLt} \tilde{P}_{\mathbf{r}', \beta} \rho(-\infty)}]. \quad (\text{A4})$$

Note that since the system is translationally invariant, after averaging over the configuration, $\chi^{(1)}$ depends on \mathbf{r} and \mathbf{r}' only through $\mathbf{r} - \mathbf{r}'$. Substituting Eq. (16) into Eq. (A4) and using $\rho(-\infty) = |0\rangle\langle 0|$ (which means the system has no exciton initially), we have

$$\chi_{\alpha\beta}^{(1)}(\mathbf{r} - \mathbf{r}', t) = \overline{i \langle \mathbf{r}, \alpha | e^{-iHt} | \mathbf{r}', \beta \rangle} + \text{c.c.} \quad (\text{A5})$$

Here c.c. denotes complex conjugate. Performing Fourier transform with respect to time, we obtain Eq. (18).

APPENDIX B: NONZERO COMPONENTS OF TENSORS IN A CUBIC CRYSTAL

In this appendix, we identify the nonzero components of tensors with cubic symmetry, i.e., the x , y , and z axes are equivalent and the tensors are invariant under the inversion of one axis. Let $T_{\alpha\beta}$ denote any second rank tensor with cubic symmetry. Since x , y , and z directions are equivalent, we have

$$T_{xx} = T_{yy} = T_{zz}. \quad (\text{B1})$$

Let us examine an off diagonal component T_{xy} . Since the system is invariant under the inversion $y \rightarrow -y$, we have

$$T_{x,y} = T_{x,-y} = -T_{x,y}, \quad (\text{B2})$$

which gives

$$T_{x,y} = 0.$$

So all off diagonal components are zero and T must be scalar, i.e.,

$$T_{\alpha\beta} = t \delta_{\alpha\beta}. \quad (\text{B3})$$

In simple cubic, fcc, and bcc lattices, the configurationally averaged 1- p Green's function $\bar{G}_{\alpha\beta}(r=0, z)$, $\bar{G}_{\alpha\beta}(k=0, z)$ and the linear susceptibility $\chi_{\alpha\beta}^{(1)}(k=0, z)$ belong to this category.

Let $T_{\alpha\beta\gamma\delta}$ denote any fourth rank tensor which is invariant under the inversion of two of the principle axes, say the y or z axis (not necessary for the x axis), then the only nonzero components are

$$T_{\alpha\alpha\beta\beta}, T_{\alpha\beta\alpha\beta}, T_{\alpha\beta\beta\alpha}, \quad \alpha, \beta = p_x, p_y, p_z.$$

For any other component, e.g., T_{xxyz} , since the system is invariant under inversion $y \rightarrow -y$, we have

$$T_{x,x,y,z} = T_{x,x,-y,z} = -T_{x,x,y,z}, \quad (\text{B4})$$

which gives

$$T_{xxyz} = 0.$$

The fourth rank tensor $L_{\alpha\beta}^{\gamma\delta}(\mathbf{q}, z_1, z_2)$ belong to this category when \mathbf{q} is along one of the principle axes (x , y , or z axis). The fourth rank tensor $A_{\alpha\beta}^{\gamma\delta}(z_1, z_2)$ [see Eq. (47)] is invariant under the inversion of the x , y , or z axis, so it also belongs to this category.

APPENDIX C: DERIVATION OF EQ. (26)

Our procedure is similar to that of Loring and Mukamel.¹¹ The third order nonlinear response function defined in Eq. (24) can be obtained from the perturbation method theory¹⁵

$$R_{\mu\alpha\mu\beta\mu\gamma}^{(3)}(\mathbf{r}t; \mathbf{r}_3 t_3, \mathbf{r}_2 t_2, \mathbf{r}_1 t_1) = \text{Tr}[\overline{P_{\mathbf{r}, \mu} e^{-iLt_3} \tilde{P}_{\mathbf{r}_3, \mu} e^{-iLt_2} \tilde{P}_{\mathbf{r}_2, \beta} e^{-iLt_1} \tilde{P}_{\mathbf{r}_1, \mu} \rho(-\infty)}]. \quad (\text{C1})$$

Here L is the Liouville operator defined in Appendix A. When the frequency of signal is off resonance, i.e., $|\omega_s - \Omega| \gg \bar{J}$, we have

$$\begin{aligned} & \int dt_3 e^{i\omega_s t_3} R_{\mu\alpha\mu\beta\mu\gamma}^{(3)}(\mathbf{r}t; \mathbf{r}_3 t_3, \mathbf{r}_2 t_2, \mathbf{r}_1 t_1) \\ &= \int dt_3 e^{i\omega_s t_3} \text{Tr}(P_{\mathbf{r}, \mu} e^{-iLt_3} Q) \\ &\approx \frac{i}{\omega_s - \Omega} \text{Tr}(B_{\mathbf{r}, \mu} Q) + \frac{i}{\omega_s + \Omega} \text{Tr}(B_{\mathbf{r}, \mu}^+ Q), \end{aligned} \quad (\text{C2})$$

where

$$Q = \tilde{P}_{\mathbf{r}_3, \mu} e^{-iLt_3} \tilde{P}_{\mathbf{r}_2, \beta} e^{-iLt_2} \tilde{P}_{\mathbf{r}_1, \mu} \rho(-\infty). \quad (\text{C3})$$

We now evaluate the first term in Eq. (C2). Using the commutation relation (5), we have

$$\begin{aligned} \text{Tr}(B_{r\mu}Q) &= \text{Tr}([B_{r\mu}, P_{r_3\mu_\alpha}]Q') \\ &= -\delta_{r,r_3}[\text{Tr}(B_{r\mu_\alpha}^+ B_{r\mu}Q') + \delta_{\mu\mu_\alpha} \text{Tr}(\hat{n}_r Q')] \end{aligned} \quad (\text{C4})$$

where

$$\begin{aligned} \text{Tr}(B_{r\mu}Q) &= \delta_{r,r_3} \left\{ \langle r\mu | \exp[-iH(t_2+t_1)] | r_1\mu_\gamma \rangle \langle r_2\mu_\beta | e^{iHt_2} | r\mu_\alpha \rangle + \delta_{\mu\mu_\alpha} \sum_{\sigma} \langle r\sigma | \exp[-iH(t_2+t_1)] | r_1\mu_\gamma \rangle \right. \\ &\quad \times \langle r_2\mu_\beta | e^{iHt_2} | r\sigma \rangle + \langle r_1\mu_\gamma | \exp[iH(t_2+t_1)] | r\mu_\alpha \rangle \langle r\mu | e^{-iHt_2} | r_2\mu_\beta \rangle \\ &\quad \left. + \delta_{\mu\mu_\alpha} \sum_{\sigma} \langle r_1\mu_\gamma | \exp[iH(t_2+t_1)] | r\sigma \rangle \langle r\sigma | e^{-iHt_2} | r_2\mu_\beta \rangle \right\} \\ &= \delta_{r,r_3} \int dE_1 \int dE_2 \left[\phi_{\mu\mu_\gamma}^{\mu\alpha\mu\beta}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}, \mathbf{r}_2, E_1+i0, E_2-i0) \exp[-iE_1(t_2+t_1)] e^{iE_2t_2} + \delta_{\mu\mu_\alpha} \sum_{\sigma} \phi_{\sigma\mu_\gamma}^{\sigma\mu\beta}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}, \mathbf{r}_2, E_1+i0, \right. \\ &\quad \left. E_2-i0) \exp[-iE_1(t_2+t_1)] e^{iE_2t_2} + \phi_{\mu\mu_\beta}^{\mu\alpha\mu\gamma}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}, \mathbf{r}_1, E_1+i0, E_2-i0) e^{-iE_1t_2} \exp[iE_2(t_2+t_1)] \right. \\ &\quad \left. + \delta_{\mu\mu_\alpha} \sum_{\sigma} \phi_{\sigma\mu_\beta}^{\sigma\mu\gamma}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}, \mathbf{r}_1, E_1+i0, E_2-i0) e^{-iE_1t_2} \exp[iE_2(t_2+t_1)] \right] / 4\pi^2. \end{aligned} \quad (\text{C7})$$

Here $\phi_{\mu\mu_\gamma}^{\mu\alpha\mu\beta}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}, \mathbf{r}_2, z_1, z_2)$ is defined in Eq. (11). Substituting Eq. (C7) into Eq. (C2) and then substituting into Eq. (25), we have

$$\begin{aligned} \chi_{\mu\mu_1\mu_2\mu_3}^{(3)}(-\mathbf{k}_s - \omega_s, \mathbf{k}_1\omega_1, -\mathbf{k}_2 - \omega_2, \mathbf{k}_3\omega_3) &= \chi_{\text{I}}^{(3)} + \chi_{\text{II}}^{(3)}, \quad (\text{C8}) \\ \chi_{\text{I}}^{(3)} &= - \sum_{\text{perm}} \int dE_1 \int dE_2 \frac{1}{4\pi^2(\omega_s - \Omega)(E_2 - E_1 + \omega_\beta + \omega_\gamma + i0)} \sum_{\mathbf{r}_1, \mathbf{r}_2} \exp[i\mathbf{k}_\beta \cdot (\mathbf{r}_2 - \mathbf{r}) + i\mathbf{k}_\gamma \cdot (\mathbf{r}_1 - \mathbf{r})] \\ &\quad \times \left[\phi_{\mu\mu_\gamma}^{\mu\alpha\mu\beta}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}, \mathbf{r}_2, E_1+i0, E_2-i0) / (\omega_\gamma - E_1 + i0) + \delta_{\mu\mu_\alpha} \sum_{\sigma} \phi_{\sigma\mu_\gamma}^{\sigma\mu\beta}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}, \mathbf{r}_2, E_1+i0, E_2-i0) / (\omega_\gamma - E_1 + i0) \right. \\ &\quad \left. + \phi_{\mu\mu_\beta}^{\mu\alpha\mu\gamma}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}, \mathbf{r}_1, E_1+i0, E_2-i0) / (\omega_\gamma + E_2 + i0) + \delta_{\mu\mu_\alpha} \sum_{\sigma} \phi_{\sigma\mu_\beta}^{\sigma\mu\gamma}(\mathbf{r}, \mathbf{r}_2, \mathbf{r}, \mathbf{r}_1, E_1+i0, E_2-i0) / (\omega_\gamma + E_2 + i0) \right]. \end{aligned} \quad (\text{C9})$$

Here $\chi_{\text{II}}^{(3)}$ denotes the contribution to $\chi^{(3)}$ from the second term in Eq. (C2). Interchanging \mathbf{r}_1 , \mathbf{r}_2 and β , γ in the third and fourth terms in the square bracket of Eq. (C9) and combining the first and the second terms, we find the first and second terms in Eq. (26). Following the same procedure, we find that $\chi_{\text{II}}^{(3)}$ in Eq. (C8) yields the third and fourth terms of Eq. (26).

APPENDIX D: CPA FOR THE 1-P GREEN'S FUNCTION

In this appendix, we use the standard CPA method¹ to derive the self-consistent equation for the configurationally averaged 1-p Green's function. Define the effective Green's function operator $\hat{G}^{\text{eff}}(z)$ and effective Hamiltonian operator $\hat{H}^{\text{eff}}(z)$ as

$$\hat{G}^{\text{eff}}(z) \equiv \frac{1}{z - \hat{H}^{\text{eff}}(z)} \equiv \bar{G}(z) \equiv \overline{(z - \hat{H})^{-1}}, \quad (\text{D1})$$

$$Q' = e^{-iLt_2} \tilde{P}_{r_2\mu_\beta} e^{-iLt_1} \tilde{P}_{r_1\mu_\gamma} \rho(-\infty). \quad (\text{C5})$$

In deriving Eq. (C4), we have used the fact

$$\text{Tr}(Q') = \text{Tr}\{[P_{r_2\mu_\beta} e^{-iLt_1} \tilde{P}_{r_1\mu_\gamma} \rho(-\infty)]\} = 0. \quad (\text{C6})$$

Substituting Eq. (C5) into Eq. (C4) and using $\rho(-\infty) = |0\rangle\langle 0|$, we have

where the caret denotes the operator. Then we can expand $(z - \hat{H})^{-1}$ as

$$\begin{aligned} (z - \hat{H})^{-1} &= \overline{[z - \hat{H}_{\text{eff}} - (\hat{H} - \hat{H}_{\text{eff}})]^{-1}} \\ &= \hat{G}^{\text{eff}}(z) + \hat{G}^{\text{eff}}(z) \hat{T}(z) \hat{G}^{\text{eff}}(z). \end{aligned} \quad (\text{D2})$$

Here the scattering operator $\hat{T}(z)$ is

$$\hat{T}(z) = [\hat{H} - \hat{H}^{\text{eff}}(z)] \{1 - \hat{G}^{\text{eff}}(z) [\hat{H} - \hat{H}^{\text{eff}}(z)]\}^{-1}. \quad (\text{D3})$$

From Eqs. (D1) and (D2), we have

$$\bar{T}(z) = 0. \quad (\text{D4})$$

This means that all matrix element of the operator $\hat{T}(z)$ are zero after the configurational average. Though Eq. (D3) and (D4) are exact, solving them exactly for $\hat{H}_{\text{eff}}(z)$ is just as difficult as calculating $\bar{G}(z)$.

In the CPA, we assume $\hat{H}^{\text{eff}}(z)$ has the form

$$\hat{H}^{\text{eff}}(z) = \sum_{\mathbf{r}, \alpha, \beta} [\Omega \delta_{\alpha\beta} + \Sigma_{\alpha\beta}(z)] B_{\mathbf{r}\alpha}^+ B_{\mathbf{r}\beta} + \sum_{\mathbf{r} \neq \mathbf{r}', \alpha, \beta} J_{\alpha\beta}(\mathbf{r} - \mathbf{r}') B_{\mathbf{r}\alpha}^+ B_{\mathbf{r}'\beta}, \quad (\text{D5})$$

where the self-energy $\Sigma_{\alpha\beta}(z)$ is a second rank tensor. For simple cubic, fcc, and bcc lattices, the self-energy tensor has cubic symmetry. In Appendix B, we prove that any second rank tensor with cubic symmetry must be a scalar (Appendix B). We thus have $\Sigma_{\alpha\beta}(z) = \Sigma(z) \delta_{\alpha\beta}$. The effective Hamiltonian becomes

$$\hat{H}^{\text{eff}}(z) = \sum_{\mathbf{r}, \alpha} [\Omega + \Sigma(z)] B_{\mathbf{r}\alpha}^+ B_{\mathbf{r}\alpha} + \sum_{\mathbf{r} \neq \mathbf{r}', \alpha, \beta} J_{\alpha\beta}(\mathbf{r} - \mathbf{r}') B_{\mathbf{r}\alpha}^+ B_{\mathbf{r}'\beta}. \quad (\text{D6})$$

It is the Hamiltonian of a regular lattice with an effective (frequency dependent) excitation energy $\Omega + \Sigma(z)$. From this, we obtain Eq. (32).

From the effective Hamiltonian (D6), we see that $\hat{H} - \hat{H}_{\text{eff}}$ is diagonal in r space

$$\hat{H} - \hat{H}^{\text{eff}}(z) = \sum_{\mathbf{r}, \alpha} [\epsilon_{\mathbf{r}\alpha} - \Omega - \Sigma(z)] B_{\mathbf{r}\alpha}^+ B_{\mathbf{r}\alpha}. \quad (\text{D7})$$

Let $\hat{T}_{\mathbf{r}}$ denote the contribution to \hat{T} by a single site \mathbf{r} , i.e.,

$$\hat{T}_{\mathbf{r}}(z) = \sum_{\alpha} [\epsilon_{\mathbf{r}\alpha} - \Omega - \Sigma(z)] B_{\mathbf{r}\alpha}^+ B_{\mathbf{r}\alpha} \left[1 - \hat{G}^{\text{eff}}(z) \sum_{\beta} [\epsilon_{\mathbf{r}\beta} - \Omega - \Sigma(z)] B_{\mathbf{r}\beta}^+ B_{\mathbf{r}\beta} \right]^{-1}, \quad (\text{D8})$$

in the CPA, the self-energy $\Sigma(z)$ will be determined self-consistently by requiring the averaged scattering operator from any single site is zero¹

$$\langle \mathbf{r}\mu | \hat{T}_{\mathbf{r}} | \mathbf{r}\mu' \rangle = 0. \quad (\text{D9})$$

Using Eq. (D8), we have

$$\langle \mathbf{r}\mu | \hat{T}_{\mathbf{r}} | \mathbf{r}\mu' \rangle = \sum_{\mu} \frac{[\epsilon_{\mathbf{r}\mu} - \Omega - \Sigma(z)]}{1 - [\epsilon_{\mathbf{r}\mu} - \Omega - \Sigma(z)] G_{\mu\mu}^{\text{eff}}(\mathbf{r}, \mathbf{r}, z)} \delta_{\mu\mu'}. \quad (\text{D10})$$

We have used the fact that the second rank tensor $G_{\mu\nu}^{\text{eff}}(\mathbf{r}, \mathbf{r}, z) \equiv \langle \mathbf{r}\mu | \hat{G}^{\text{eff}}(z) | \mathbf{r}\nu \rangle$ is a scalar (Appendix B), i.e.,

$$G_{\mu\nu}^{\text{eff}}(\mathbf{r}, \mathbf{r}, z) \equiv \langle \mathbf{r}\mu | \hat{G}^{\text{eff}}(z) | \mathbf{r}\nu \rangle = G_{\mu\mu}^{\text{eff}}(\mathbf{r}, \mathbf{r}, z) \delta_{\mu\nu}, \quad (\text{D11})$$

where $G_{\mu\mu}^{\text{eff}}(\mathbf{r}, \mathbf{r}, z)$ is independent of μ and \mathbf{r} (due to cubic symmetry and translational invariance),

$$\begin{aligned} G_{\mu\mu}^{\text{eff}}(\mathbf{r}, \mathbf{r}, z) &= \frac{1}{3M} \sum_{\mathbf{r}, \mu} \langle \mathbf{r}\mu | \hat{G}^{\text{eff}}(z) | \mathbf{r}\mu \rangle \\ &= \frac{1}{3M} \text{Tr} \left[\frac{1}{z - \hat{H}^{\text{eff}}(z)} \right] \\ &= \int d\epsilon \frac{N^0(\epsilon)}{z - \Sigma(z) - \epsilon}. \end{aligned} \quad (\text{D12})$$

Here \hat{H}_0 and $N^0(E)$ are the Hamiltonian and density of states of the regular lattice ($c=1$) given by Eqs. (36) and (37). Substituting Eq. (D10) into Eq. (D9) and using Eq. (3), we obtain the self-consistent equation (34).

APPENDIX E: EVALUATION OF LATTICE DIPOLE SUMS

The procedure of calculating $J_{\mu\nu}(\mathbf{k})$ is described in Ref. 17. We quote the final result here

$$\begin{aligned} J_{\mu\nu}(\mathbf{k}) &= -4\pi^2 \tau^{5/2} [S_C + S_D + (2\pi\tau)^{-1} (\frac{2}{3} - S_A) \delta_{\mu\nu}], \\ S_C &= \sum_{l \neq 0} [r_l^\mu r_l^\nu \exp(i\mathbf{k} \cdot \mathbf{r}_l) \varphi_{3/2}(\tau r_l^2 \pi)], \\ S_D &= -\frac{1}{4v\pi^2 \tau^{7/2}} \sum_l \{ (2\pi b_l^\mu - k^\mu) (2\pi b_l^\nu - k^\nu) \\ &\quad \times \varphi_0[(2\pi b_l - \mathbf{k})^2 / 4\pi\tau] \}, \\ S_A &= \sum_{l \neq 0} [\exp(i\mathbf{k} \cdot \mathbf{r}_l) \varphi_{1/2}(\tau r_l^2 \pi)]. \end{aligned} \quad (\text{E1})$$

Here S_A and S_C are summed over direct lattice \mathbf{r}_b , S_D is summed over reciprocal lattice b_b , v is the volume of unit cell, and τ is arbitrary which is chosen to make the summation in both direct and reciprocal space to converge rapidly. For a fcc lattice, the basis vectors of the unit cell are $(0,1,1)$, $(1,0,1)$, and $(1,1,0)$ for the direct lattice, and $(\frac{-1}{2}, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, \frac{-1}{2}, \frac{1}{2})$, and $(\frac{1}{2}, \frac{1}{2}, \frac{-1}{2})$ for the reciprocal lattice. The φ functions are given by

$$\varphi_m(x) = \int_1^\infty \beta^m e^{-\beta x} d\beta. \quad (\text{E2})$$

For $m=0, 1/2$, and $3/2$, we have

$$\begin{aligned} \varphi_0(x) &= e^{-x}/x, \\ \varphi_{1/2}(x) &= e^{-x}/x + \sqrt{\frac{\pi}{4x^3}} [1 - \text{erf}(\sqrt{x})], \\ \varphi_{3/2}(x) &= (1 + 3/2x) e^{-x}/x + \frac{3}{4x^2} \sqrt{\frac{\pi}{x}} [1 - \text{erf}(\sqrt{x})]. \end{aligned} \quad (\text{E3})$$

Here $\text{erf}(x)$ is Gauss' error function.

APPENDIX F: THE LADDER DIAGRAM APPROXIMATION

In this appendix, we calculate $\phi_{\mu\mu_1}^{\mu_3\mu_1}[(\mathbf{k}_1 + \mathbf{k}_2)/2, \mathbf{k}_1 - \mathbf{k}_2, z_1, z_2]$ using the ladder diagram approximation. Summing over \mathbf{p} on both sides of the Bethe-Salpeter equation (46), using Eq. (47) and putting $\alpha = \mu$, $\beta = \gamma = \mu_1$, $\sigma = \mu_3$, $\mathbf{p}' = (\mathbf{k}_1 + \mathbf{k}_2)/2$, and $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$, we have

$$\begin{aligned} &\phi_{\mu\mu_1}^{\mu_3\mu_1}[(\mathbf{k}_1 + \mathbf{k}_2)/2, \mathbf{k}_1 - \mathbf{k}_2, z_1, z_2] \\ &= \bar{G}_{\mu\mu_1}(\mathbf{k}_1, z_1) \bar{G}_{\mu_1\mu_3}(\mathbf{k}_2, z_2) \\ &\quad + \sum_{\alpha', \beta', \sigma', \gamma'} L_{\mu\alpha'}^{\mu_3\sigma'}(\mathbf{k}_1 - \mathbf{k}_2, z_1, z_2) A_{\alpha'\beta'}^{\sigma'\gamma'}(z_1, z_2) \\ &\quad \times \phi_{\beta'\mu_1}^{\gamma'\mu_1}[(\mathbf{k}_1 + \mathbf{k}_2)/2, \mathbf{k}_1 - \mathbf{k}_2, z_1, z_2]. \end{aligned} \quad (\text{F1})$$

The fourth rank tensor $L_{\alpha\beta}^{\sigma\gamma}(\mathbf{q}, z_1, z_2)$ is defined in Eq. (50). If $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$ is along one of the principle axes of the cubic lattice, say the x axis, then the fourth rank tensor $L_{\alpha\beta}^{\sigma\gamma}$ is

invariant under the inversion of the y or z axis. From Appendix B, we know that the only nonzero components of L are

$$L_{\alpha\alpha}^{\beta\beta}, L_{\alpha\beta}^{\alpha\beta}, L_{\alpha\beta}^{\beta\alpha}, \quad \alpha, \beta = p_x, p_y, p_z.$$

We now show that $\phi_{\mu\mu_1}^{\mu_3\mu_1}$ is nonzero only when $\mu = \mu_3$. Iterating Eq. (F1), we have

$$\begin{aligned} & \phi_{\mu\mu_1}^{\mu_3\mu_1}[(\mathbf{k}_1 + \mathbf{k}_2)/2, \mathbf{k}_1 - \mathbf{k}_2, z_1, z_2] \\ &= \bar{G}_{\mu\mu_1}(\mathbf{k}_1, z_1) \bar{G}_{\mu_1\mu_3}(\mathbf{k}_2, z_2) \\ &+ \sum_{\alpha', \beta', \sigma', \gamma'} L_{\mu\alpha'}^{\mu_3\sigma'}(\mathbf{k}_1 - \mathbf{k}_2, z_1, z_2) \\ &\times A_{\alpha'\beta'}^{\sigma'\gamma'}(z_1, z_2) \bar{G}_{\beta'\mu_1}(\mathbf{k}_1, z_1) \bar{G}_{\mu_1\gamma'}(\mathbf{k}_2, z_2) + \dots \quad (\text{F2}) \end{aligned}$$

Suppose the external field E_1, E_2 are transverse, i.e., $\mathbf{k}_1 \perp \hat{\mu}_1, \mathbf{k}_2 \perp \hat{\mu}_1$, and condition (39) holds, we know from Eqs. (32) and (40) that $\bar{G}_{\alpha\mu_1}(\mathbf{k}_1, z_1)$ and $\bar{G}_{\beta\mu_1}(\mathbf{k}_2, z_2)$ are nonzero only if $\alpha = \mu_1, \beta = \mu_1$. We see that the first term in the above equation is nonzero only if $\mu = \mu_3 = \mu_1$, the second term is nonzero only if $\beta' = \gamma' = \mu_1$, which in turn requires $\sigma' = \alpha'$ to make A nonzero, which in turn requires $\mu_3 = \mu$ to make L nonzero. So the second term is nonzero only if $\mu = \mu_3$. Following this procedure, we can prove that all the higher order terms in the above equation are zero whenever $\mu \neq \mu_3$. So we have shown that $\phi_{\mu\mu_1}^{\mu_3\mu_1}[(\mathbf{k}_1 + \mathbf{k}_2)/2, \mathbf{k}_1 - \mathbf{k}_2, z_1, z_2]$ is nonzero only if $\mu = \mu_3$. The same is true for $\phi_{\mu_3\mu_1}^{\mu\mu_1}[(\mathbf{k}_1 + \mathbf{k}_2)/2, \mathbf{k}_1 - \mathbf{k}_2, z_1, z_2]$. From Eq. (31) we see that $\chi_{\mu\mu_3\mu_1\mu_1}^{(3)}(-\mathbf{k}_s - \omega_s \mathbf{k}_1 \omega_1, -\mathbf{k}_2 - \omega_2 \mathbf{k}_3 \omega_3)$ is nonzero only if $\mu = \mu_3$.

Now we calculate $\phi_{\mu_3\mu_1}^{\mu\mu_1}[(\mathbf{k}_1 + \mathbf{k}_2)/2, \mathbf{k}_1 - \mathbf{k}_2, z_1, z_2]$. Setting $\mu = \mu_3$ in Eq. (F1), we see that the second term in Eq. (F1) is nonzero only if $\sigma' = \alpha', \gamma' = \beta'$. It is convenient to define the 3 by 3 matrix $L(\mathbf{q}, z_1, z_2), A(z_1, z_2)$ whose $\alpha\beta$ matrix elements are $L_{\alpha\beta}^{\alpha\beta}(\mathbf{q}, z_1, z_2), A_{\alpha\beta}^{\alpha\beta}(z_1, z_2)$; then Eq. (F1) gives Eq. (51) directly.

Now we determine the matrix $A(z_1, z_2)$ self-consistently. Summing over \mathbf{p} and \mathbf{p}' on both sides of the Bethe-Salpeter equation (46) and setting $\sigma = \alpha, \gamma = \beta$, we have

$$\begin{aligned} \phi_{\alpha\beta}^{\alpha\beta}(\mathbf{q}, z_1, z_2) &= L_{\alpha\beta}^{\alpha\beta}(\mathbf{q}, z_1, z_2) \\ &+ \sum_{\alpha'\beta'} L_{\alpha\alpha'}^{\alpha\alpha'}(\mathbf{q}, z_1, z_2) A_{\alpha'\beta'}^{\alpha'\beta'}(z_1, z_2) \phi_{\beta'\beta}^{\beta'\beta}(\mathbf{q}, z_1, z_2), \quad (\text{F3}) \end{aligned}$$

which gives Eq. (60) immediately. Here $\phi_{\alpha\beta}^{\alpha\beta}(\mathbf{q}, z_1, z_2)$ is defined in Eq. (59). From this definition together with Eqs. (6) and (11), we can derive

$$\begin{aligned} & \sum_{\beta} \phi_{\alpha\beta}^{\alpha\beta}(q=0, z_1, z_2) \\ &= \frac{1}{M} \sum_{\mathbf{r}_1, \mathbf{r}_2, \beta} \langle \mathbf{r}_1 \alpha | \frac{1}{z_1 - H} | \mathbf{r}_2 \beta \rangle \langle \mathbf{r}_2 \beta | \frac{1}{z_2 - H} | \mathbf{r}_1 \alpha \rangle \\ &= \frac{1}{M} \frac{1}{z_1 - z_2} \sum_{\mathbf{r}_1} \langle \mathbf{r}_1 \alpha | \frac{1}{z_2 - H} \frac{1}{z_1 - H} | \mathbf{r}_1 \alpha \rangle \\ &= \frac{G_{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_1, z_2) - G_{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_1, z_1)}{z_1 - z_2}. \quad (\text{F4}) \end{aligned}$$

Equation (F4) is an exact relation between the configurationally averaged p - h Green's function and configurationally averaged 1 - p Green's function; we will call it the Ward identity.¹³ Note in deriving the Ward identity, we use the fact that our Hamiltonian conserves the number of excitons, so the single exciton states $|\mathbf{r}_2\beta\rangle$ are complete basis sets given that the initial state $|\mathbf{r}_1\alpha\rangle$ is a single exciton state

$$\sum_{\mathbf{r}_2\beta} |\mathbf{r}_2\beta\rangle \langle \mathbf{r}_2\beta| = 1.$$

Substituting Eq. (60) into Eq. (F4), we obtain the self-consistent equation for the matrix $A(z_1, z_2)$ [Eq. (52)].

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