Theory of resonant modes in particulate matter

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A theory for the resonant excitation of a system of particles is presented. Infinite series arising from the multiple couplings are converted into simple expressions involving only determinants that allow for easy numerical evaluation of the resonances up to high order in the multipoles included. Linear, planar, and cubic arrangements of dielectric spheres are analyzed, and they all indicate a failure of the dipole approximation when the particles are closer than about three particle radii from each other. A convergence criterion as a function of interparticle separation for smaller distances is provided. In particular, it is found that some geometries in which particles touch require multipoles to all orders for a proper evaluation of resonant modes. It is shown that dimensionality is not important for excitation along a long dimension of the arrangement. Results for NaCl spheres are presented, and the effect of the above findings on their optical spectrum is analyzed.

I. INTRODUCTION

The physical properties of small particles have been the subject of much recent interest. In particular the effect of shape and environment has been studied through their response to an electromagnetic excitation. The first influences the polarizability and the second the local field each particle is in. It is well known that an isolated uniform dielectric sphere, for instance, exhibits an absorption resonance in the long-wavelength limit for a material dielectric constant value of $\epsilon=-2$, far away from the bulk resonance.[1,2] By contrast the corresponding resonance in a rectangular particle may be shifted through the whole range $-\infty<\epsilon\leq 0$ by changing the extensions of the parallelepiped.[3] These examples illustrate the effect of shape. The effect of the environment may be exemplified by taking a uniform sphere and observing its optical spectra as an identical sphere is approached along the direction of polarization of the field. The result is that there is not one but several resonances whose location depends on the particle separation and cover with it the whole range $-\infty<\epsilon<-1$.[4,5] Thus shape and environment of particles are important in analyzing the properties of particulate matter. Optical properties as well as the dynamics of their motion are influenced by them.[6–8] We note also that in the limit of very small particles with radii ~ 100 Å size may also be a dominant consideration.[9–12]

In this work we are interested in the effect of the environment. In particular we treat the case of a particle in the presence of one or more particles in the static approximation, that is, for an excitation whose wavelength is much larger than the particle diameter and interparticle separation. Shape and bulk properties are introduced through the particles polarizabilities. A satisfactory solution to this problem is not necessarily simple since it must be self-consistent in the sense that the effect of environment on a given particle changes the response of the environment itself. Also there is the question of convergence in the multipole couplings between particle and environment that occur. The validity of the usual dipole approximation[13,14] has been questioned by several authors when the particles are very close[15–18] and calculations done including higher multipoles confirm this view.[4,5,17–27] The suggestion that the approximation holds up to an interparticle separation of about three-particle radii has been made based first on numerical evidence for two identical particles[4,17] and later extended to a string and a square lattice.[5]

Going beyond the dipole approximation is not trivial since self-consistency requires the summation of an infinite series for each new coupling treated. This difficulty has limited progress in the assessment of the importance of multipolar effects. We develop here a theory that yields a straightforward computational scheme for obtaining the normal modes of the system to an arbitrary pole order assuming only that the polarizabilities are known. This is done in Sec. II. In Sec. III we discuss optically active modes for a system of 2, 3, and infinite identical particles arranged along a line, or a lattice in two and three dimensions. This allows us to study the effect of dimensionality on the spectrum of resonances. Numerical results for such geometries are obtained in Sec. IV, where we treat the special case of uniform dielectric spheres. We end with a summary and conclusions in Sec. V.

II. THE NORMAL MODES EQUATION

We consider a set of N polarizable charge distributions (particles) that are nonoverlapping, but otherwise arbitrary. The system obeys the usual laws of electrodynamics, whatever the mechanisms of response within a particle to an external drive may be. These could be pure phonon or polariton modes in a dielectric,[28] or pure electron response as in a metal[29] or an atom,[22] for example. The response of any particle, for example, the ith one, is characterized by the polarizabilities α_{lmi}, which we take to be defined by the relation[30]

$$q_{lmi}=-\frac{2l+1}{4\pi}\alpha_{lmi}V_{lm}(i)\ , \tag{1}$$

where

$$q_{lmi}=\int \rho_i(\vec{r})[Y_l^m(\theta,\psi)]^* d\vec{r}$$

is the (l,m) moment of the charge distribution ρ_i, and $V_{lm}(i)$ is the expansion coefficient, of order (l,m), of the potential the particle is in, the potential and integral having the same origin within the particle. If the particle is isolated the potential is just the applied external field, if present, but if more particles are around, their excitation will modify the field at the site of the ith particle. The complete potential is then a sum containing the external field and the contribution from every other particle present in the system. We shall ignore retardation effects, which means that field wavelengths are larger than the relevant dimensions of the system. The (l,m) component of the potential may then be written in the form

$$V_{lm}(i)=V_{lm}^{\text{ext}}(i)+\sum_{\substack{i,j\\ j\neq i}} V_{lm}^j(i) . \tag{2}$$

From the multipole expansion of the field due to the jth, particle we obtain[22]

$$V_{lm}^j(i)=\sum_{l',m'}(-1)^{l'}A_{lmi}^{l'm'j}q_{l'm'j} , \tag{3}$$

where the geometrical coefficients

$$A_{lmi}^{l'm'j}=(-1)^{m'}\left[\frac{(4\pi)^3}{(2l+1)(2l'+1)(2l+2l'+1)}\frac{(l+l'+m-m')!(l+l'-m+m')!}{(l'+m')!(l+m)!(l'-m')!(l-m)!}\right]^{1/2}\frac{[Y_{l+l'}^{m-m'}(\theta_{ij},\varphi_{ij})]^*}{R_{ij}^{l+l'+1}} \tag{4}$$

obey the symmetry relations in the respective indices

$$A_{lm}^{lm}=A_{lm}^{l'm} , \tag{5}$$

$$A_{lm'}^{lm}=(A_{lm}^{lm'})^*=(-1)^{m+m'}(A_{l-m'}^{l-m})^* , \tag{6}$$

and

$$A_j^i=(-1)^{l+l'}A_i^j . \tag{7}$$

Here $\vec{R}_{ij}=(R_{ij},\theta_{ij},\varphi_{ij})$ is the vector from the origin at the ith particle to the origin at the jth particle. Replacing in (1) we get the set of coupled linear equations for the moments

$$q_\mu=F_\mu+\sum_{\mu'}B_\mu^{\mu'}q_{\mu'} \tag{8}$$

that constitute the basic equations of this paper. We have used the compact notation $\mu=(l,m,i)$,

$$F_\mu=-\frac{2l+1}{4\pi}\alpha_{lmi}V_{lm}(i) , \tag{9}$$

and

$$B_\mu^{\mu'}=(-1)^{l'+1}\frac{2l+1}{4\pi}\alpha_{lmi}A_{lmi}^{l'm'i'} \tag{10}$$

in order to simplify the expressions. The sum runs over all possible values of the triplet μ' ($l'=0,1,\ldots$; $m'=-l',-l'+1,\ldots,l'$; $i'=1,2,\ldots,N$) if we adopt the convention $B_{lmi}^{l'm'i}=0$. Physically the coefficient $B_\mu^{\mu'}$ represents the direct coupling strength of the moment of order (l,m) of the ith particle with the moment of order (l',m') in the ith particle so that our convention just states that a particle does not couple directly with itself. It can certainly couple with itself with the intermediacy of other particles however, as we shall see below. A special case of Eq. (8) valid for spherical dielectric particles was previously derived by Gérardy and Ausloos.[16]

In principle, Eq. (8) constitutes an infinite set of equations. The couplings become weaker as the indices l,l' become larger, however, and it is reasonable to cut off the infinite sequence $l=0,1,\ldots$ at some $l_{\max}=L$. This simplification defines what we will call the 2^L-pole approximation ($L=1$, dipole; $L=2$, quadrupole; $L=3$, octupole; etc.). Thus in the dipole approximation for uncharged particles only dipole moments appear in Eq. (8) and we have in general a set of (at most) $3N$ linear equations that may be easily solved using Kramers rule. We expect this approximation to be good provided the particles are far apart and the external field does not vary significantly within the dimensions of the system. In the quadrupole approximation Eq. (8) will mix dipole and quadrupole moments, and the number of equations to solve increases to (at most) $8N$. In the 2^L-pole case the number is $L(L+2)N$, so that it grows as L^2 for large L. This shows that going beyond the dipole approximation can be costly in computing time. Symmetry properties of the particles and their arrangement eliminates certain couplings, making the set of equations separable and thus reducing the dimensionality of the problem. In choosing our examples below we shall draw heavily on this simplification in order to go as far as possible in the size of L.

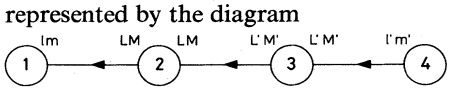
Iteration of Eq. (8) yields an expression that is physically instructive. It reads

$$q_\mu=F_\mu+\sum_{\mu'}{}' Q_\mu^{\mu'}F_{\mu'}+Q_\mu^\mu q_\mu , \tag{11}$$

where

$$Q_\mu^{\bar{\mu}}=B_\mu^{\bar{\mu}}+\sum_{\nu}{}' B_\mu^\nu B_\nu^{\bar{\mu}}+\sum_{\nu,\nu'}{}' B_\mu^\nu B_\nu^{\nu'}B_{\nu'}^{\bar{\mu}}+\cdots , \tag{12}$$

and the prime in a sum means that the summation indices skip the set μ. One may interpret now the quantity $Q_\mu^{\bar{\mu}}$ defined by the sum (12) as the complete coupling strength of particle i through its (l,m) moment, to the $(\bar{l},\bar{m})$ moment of particle $\bar{i}$. The first term is the direct coupling; the second, the coupling through the intermediacy of an excitation in any particle of the system, summed over all possible sets not including (l,m,i); the third, the coupling through the intermediacy of two particles, and so on. For instance, the term in the third sum $B_{lm1}^{LM2}B_{LM2}^{L'M'3}B_{L'M'3}^{l'm'4}$ may be represented by the diagram



meaning that the particle 4 is coupled to 1 through excitations in 3 and 2 involving the moments that label each interaction line. With this interpretation the first term in (11) gives the direct coupling to the external field, the second the coupling to other external field components through their action on different sets $\mu'=(l',m',i')$, and the third is a self-polarization term. An especially simple form of (11) occurs when the external field is uniform. The field components for $l\neq 1$ are all zero, and after some rearrangement we obtain

$$q_{1mi}=F_{1m}+\frac{\sum_{m',i'} Q_{1mi}^{1m'i'}F_{1m'}}{1-Q_{1mi}^{1mi}}, \tag{13}$$

$$q_{lmi}=\frac{\sum_{m',i'} Q_{lmi}^{1m'i'}F_{1m'}}{1-Q_{lmi}^{lmi}}. \tag{14}$$

The particle index in the field has been omitted since this quantity is in this case the same at all particle positions. Notice that except for cases in which symmetry suppresses some couplings, all moments are excited by an external field, not just the dipole. This fact is important in what follows. Notice also that if different values of m are not mixed in Eq. (13), as is the case in symmetric arrangements of spherical particles, one may define an effective dipole polarizability

$$\bar{\alpha}_{1mi}=\frac{1+\sum_{i}{}' Q_{1mi}^{1mi'}}{1-Q_{1mi}^{1mi}}\alpha_{1mi}. \tag{15}$$

Normal modes are the solutions of Eq. (11) with the field set to zero, that is, they are defined through the condition

$$Q_{\mu}^{\mu}=1. \tag{16}$$

Even in the dipole approximation this equation for the self-polarization factor is difficult to solve since it requires the evaluation of the infinite series (12). An alternate expression for the sum derived in the Appendix simplifies the problem greatly. From (A4), Eq. (16) may be written in the form

$$\frac{\det(\underline{B}-\underline{I})}{\mathrm{cof}(B_{\mu}^{\mu}-1)}=0 \tag{17}$$

where $\underline{B}$ is the matrix formed by the elements $B_{\mu}^{\bar{\mu}}$, and $\underline{I}$ is the unit matrix. The problem is thus reduced to computing determinants of (at most) size $NL(L+2)$ and solving for the resonances. The number of resonances equals that of each particle when isolated, summed over all particles in the system. This can be seen by noting that when the particles are very far apart from each other the left-hand side of (17) approaches the inverse of the single-particle polarizability α_{lmi}, so that the number of poles of this quantity summed over all possible triplets (l,m,i) determines the total number of modes at all separations. Condition (17) amounts in general to finding a zero of the determinant of matrix $\underline{B}-\underline{I}$, a solution that remains valid for all values of μ. The normal mode associated with such solution is then an excitation of the system as a whole. When symmetry suppresses couplings then the denominator plays a role, causing cancellations for certain values of μ. Uncoupled sets in the system are then excited independently and the corresponding normal modes for a given set will not involve modes of the other set.

Normal modes are suppressed by damping. A collective mode may still be excited by an external field in such a situation and will appear as a resonance in the spectrum. These collective modes are associated with ordinary normal modes and the correspondence is established by letting the damping term approach zero. Such modes are called active modes of the system.

We are interested in the absorption of electromagnetic waves by particles in the long-wavelength limit and in the absence of magnetic effects. The absorption cross section in an external electric field $\vec{E}$ is then given by[31]

$$\sigma=\frac{(4\pi)^2\omega}{3c}\,\mathrm{Im}\sum_{i=1}^{N}\left[\frac{\bar{\alpha}_{11i}+\bar{\alpha}_{1-1i}}{2}\sin^2\epsilon+\bar{\alpha}_{10i}\cos^2\epsilon\right], \tag{18}$$

where the effective dipole polarizabilities are given by (15), ϵ is the angle the electric field makes with the z axis, and ω is the frequency. In the next section we shall give explicit expressions for a few arrangements of identical particles.

III. OPTICALLY ACTIVE MODES

In an external field normal modes appear as peaks in the absorption spectrum. Not every normal mode gives a peak, however, since the field couples to the system through the dipole moment, and as is clear from Eqs. (13) and (17) cancellations could make the latter a smooth function around certain modes. Collective modes that make the dipole moment resonant are the so-called optically active (OA) modes of the system. In the presence of damping the peaks become finite and broaden but may still be seen depending on how strong and damping is, and on geometry. We shall consider next a few simple examples that will allow us to illustrate and analyze the properties of these modes. Only identical particles will be treated for simplicity although the extension to more than one kind can easily be done. In this section we derive the general expressions and leave numbers for next section, where we will take a concrete model for the polarizabilities.

A. $N=2$

Consider two identical particles with their centers a distance D apart and placed on the z axis. From (4) and the properties of spherical harmonics it follows that the coupling strength involving unequal values of m between the particles is zero. The set of equations (8) does not mix values of m, and for each value of this integer there is a closed set that may be solved independently. Whenever only two indices are shown below it means that the index m has been omitted.

It is convenient to discuss this case in terms of the coefficients $P_{li}^{l'i'}$ that represent the coupling of the l moment

of particle i to the l' moment of particle i' through all possible intermediate pairings not involving moment l, as defined in the appendix. From (A7), (5), and (10), one can readily verify the symmetry properties $P_{l1}^{l1}=P_{l2}^{l2}$ and $P_{l1}^{l2}=P_{l2}^{l1}$. Using these results in (A11) yields

$$Q_{l1}^{l1}=1+\frac{(1-P_{l1}^{l1}-P_{l1}^{l2})(1-P_{l1}^{l1}+P_{l1}^{l2})}{P_{l1}^{l1}-1}\ , \tag{19}$$

which also equals Q_{l2}^{l2}. According to (16) normal modes occur whenever any of the factors in parentheses above vanish. We shall see that the zeroes of the first factor in parentheses for $l=1$ define the OA modes of this system. Again from (A7) follows

$$Q_{l1}^{l1}+Q_{l1}^{l2}=\frac{(P_{l1}^{l1}+P_{l1}^{l2})(1-P_{l1}^{P1}+P_{l1}^{l2})}{1-P_{l1}^{l1}}\ . \tag{20}$$

The above expressions may be used in (13) to obtain the dipole polarization. We get for either particle

$$q_{1m}=\frac{F_{1m}}{1-P_{11}^{11}-P_{11}^{12}}\ . \tag{21}$$

The zeroes of the first factor in parentheses in (19) thus determine the OA modes, the other modes being given by the zeroes of the second factor in parentheses. Explicit expressions for these brackets may be obtained with the aid of (A7) and (A4). One obtains

$$1-P_{l1}^{l1}\pm P_{l1}^{l2}=-\frac{\det(\underline{M}-\underline{I})}{\mathrm{cof}(M_l^l-1)}\ , \tag{22}$$

where $\underline{I}$ is the unit matrix, and $\underline{M}$ has the elements

$$M_k^{k'}=\mp N_{km}^{k'm}\frac{\alpha_{km}}{D^{k+k'+1}}\ , \tag{23}$$

with[32]

$$N_{km}^{k'm}=(-1)^{l+m+1}\times\frac{(k+k'+m-m')!}{[(k+m)!(k-m)!(k'+m')!(k'-m')!]^{1/2}}\ . \tag{24}$$

The vanishing of (22) requires the determinant to be zero,

$$\det(\underline{M}-\underline{I})=0\ . \tag{25}$$

To order L it is simply an $L\times L$ determinant and the normal modes may be found to high-pole order without much computational effort. Because of the dependence on D of the matrix elements (23), as the particles are drawn apart couplings of high order become less and less important. Equation (22) may in fact be viewed as a perturbation series in D^{-1} cut at order $L(L+2)$. For OA modes the moments of particles 1 and 2 are related through $q_{l1}=(-1)^{l+1}q_{l2}$ whereas for inactive modes $q_{l1}=(-1)^l q_{l2}$ holds. Notice that for OA modes the dipole moments ($l=1$) of the particles are parallel and equal whereas for inactive modes they are antiparallel.

B., Three particles aligned

Consider next three identical particles labeled 1,2,3 placed on the z axis at the origin, $z=D$ and $2D$, respectively. This case is similar to the $N=2$ case, only that now the particle at the center gives rise to additional modes. For OA modes the excitations of particles 1 and 3 obey $q_{l1}=(-1)^{l+1}q_{l3}$ whereas for particle 2, $q_{l2}=0$ for l even. The dipole polarization is different from zero for the three particles and thus they all contribute to absorption, the one at the center giving a different contribution from the other two. Inactive modes, in contrast obey $q_{l1}=(-1)^l q_{l3}$ and $q_{l2}=0$, l odd. To find the OA modes, one must solve (25), where now the matrix $\underline{M}$ has elements which are themselves 2×2 matrices,

$$\underline{M}_k^{k'}=(-1)^{k+1}N_{km}^{k'm}\frac{\alpha_{km}}{D^{k+k'+1}}\begin{bmatrix}\frac{1}{2^{k+k'+1}} & (-1)^{k'+1}\\ 1-(-1)^k & 0\end{bmatrix}\ . \tag{26}$$

C. Infinite lattice

We now turn to the case of a lattice arrangement of identical particles. This case is convenient to study the effect of dimensionality since it gives transparent and simple results. The treatment that follows can be easily extended to a lattice with a basis of possibly unequal particles. Equation (16) may be transformed with the aid of (A11) into the simpler condition

$$\frac{\det(\underline{P}-\underline{I})}{\mathrm{cof}(P_i^i-1)}=0\ , \tag{27}$$

where the elements of the matrix P are $P_j^{j'}\equiv P_{lmj}^{lmj'}$ as given by (A7). If in the determinant we add all other columns to the ith column, the quantity $\sum_{j=1}^{\infty}P_l^j-1$ comes out as a factor since it is independent of i. Setting this quantity to zero gives the OA modes of the system as may be checked directly from Eq. (8) by noting that by symmetry excitations are the same in all particles. The identity

$$\sum_{j=1}^{\infty}P_l^j-1=\frac{\det(\underline{M}-\underline{I})}{\mathrm{cof}(M_{lm}^{lm}-1)} \tag{28}$$

reduces the condition for OA modes to Eq. (25), where the elements of $\underline{M}$ are now given by

$$M_{lm}^{l\bar{m}}=\sum_{i'=1}^{\infty}B_{lmi}^{l\bar{m}i'}\ . \tag{29}$$

Explicit expressions may be given for a few simple cases. One may rewrite (29) in the form

$$M_{lm}^{l\bar{m}}=G_{lm}^{l\bar{m}}\frac{\alpha_{lm}}{D^{l+\bar{l}+1}}\ , \tag{30}$$

where D is the lattice parameter and G is a factor of purely geometric nature that is given by

$$G_{lm}^{l\bar{m}}=2N_{lm}^{l\bar{m}}\xi(l+\bar{l}+1)\Delta_{l\bar{l}}\delta_{m\bar{m}} \tag{31}$$

for the linear chain,

$$G_{lm}^{\bar{l}\bar{m}}=\bar{N}_{lm}^{\bar{l}\bar{m}}\left[\xi(l+\bar{l}+1)+\sum_{n,n'=1}^{\infty}\frac{T_{m-\bar{m}}(n,n')}{[n^2+(n')^2]^{(l+\bar{l}+1)/2}}\right]\Delta_{l\bar{l}}\bar{\Delta}_{m\bar{m}} \tag{32}$$

for the square lattice, and

$$G_{lm}^{\bar{l}\bar{m}}=\bar{N}_{lm}^{\bar{l}\bar{m}}\left[(1+\tfrac{1}{2}\delta_{m,\bar{m}})\xi(l+\bar{l}+1)+\sum_{n,n'=1}^{\infty}\frac{T_{m-\bar{m}}(n,n')+2R_{l+\bar{l}}^{m-\bar{m}}(n,0,n')}{[n^2+(n')^2]^{(l+\bar{l}+1)/2}}+\sum_{n,n',n''=1}^{\infty}\frac{2T_{m-\bar{m}}(n,n')R_{l+\bar{l}}^{m-\bar{m}}(n,n',n'')}{[n^2+(n')^2+(n'')^2]^{(l+\bar{l}+1)/2}}\right]\Delta_{l\bar{l}}\bar{\Delta}_{m\bar{m}} \tag{33}$$

for the simple cubic lattice. In these expressions $\xi(k)$ is Riemann's zeta function, $\Delta_{kk'}$ ($\bar{\Delta}_{kk'}$) equals 1 if $k-k'$ is even (a multiple of 4), and 0 otherwise. Also, the coefficient N is given by (24) and

$$\bar{N}_{lm}^{\bar{l}\bar{m}}=(-1)^{(l+\bar{l})/2}\frac{N_{lm}^{\bar{l}\bar{m}}(l+\bar{l}-m+\bar{m})!}{2^{l+\bar{l}-2}[(l+\bar{l}+m-\bar{m})/2]![(l+\bar{l}-m+\bar{m})/2]!},$$

$$T_{2k}(n,n')=\frac{1}{[n^2+(n')^2]^k}\sum_{s=0}^{k}(-1)^s\binom{2k}{2s}n^{2k-2s}(n')^{2s},$$

$$R_l^m(n,n',n'')=\frac{P_l^m\left(\dfrac{n''}{[n^2+(n')^2+(n'')^2]^{1/2}}\right)}{P_l^m(0)},$$

with $P_l^m(x)$ in this last expression, the associated Legendre function. The z axis has been chosen to point along the linear chain, normal to the square lattice plane and along one of the principal directions of the cubic lattice. In actual computations simplifications occur due to the appearance of the Δ function in these expressions. It means, for instance, that the dipole moment does not couple to multipoles of even order so that in fact the determinant in (27) may be broken down into two factors, one involving only even orders and the other, multipoles of odd order. The OA modes are then found solving for the zeroes of the latter factor.

IV. THE CASE OF DIELECTRIC SPHERES

We have said nothing so far concerning the detailed manner of response of the particles the medium is composed of. In the previous formulas their physical properties appear through the polarizabilities which are still to be specified. For definiteness we assume in this section the system to be made of uniform dielectric spheres, a case often treated in the literature because of its simplicity. The optical properties of periodic arrays of such spheres for wavelengths comparable to the interparticle distance have been studied by Ohtaka and Inoue.[6,7] The polarizabilities are independent of the index m and are given by

$$\alpha_{lm}=\frac{l(\epsilon-1)}{l(\epsilon+1)+1}a^{2l+1}, \tag{34}$$

where a is the sphere radius and ϵ the dielectric constant. Normal modes occur for special values of ϵ that we label ϵ^*, defined through Eq. (16) or its special forms, Eqs. (17), (25), and (27). Mode frequencies are then given by the dispersion relation of the material once these values of ϵ are known. We have done numerical work using this model. Our main interest here is in OA modes, their dependence on geometry and dimensionality, and the convergence properties of the multipolar expansion. We shall present results obtained from the various configurations of particles discussed in Sec. III. In none of these configurations are the dipole moments $q_{1M}(M=0,\pm1)$ coupled to each other so we shall label our results by the value of M treated in each case. This index acquires its meaning from the orientation of the z axis implicit in the formulas of Sec. III.

Figure 1 shows our results for ϵ^* at the first few modes as a function of separation for the two spheres case. Figure 1(a) is for an external field parallel to the line joining the centers ($M=0$), and Fig. 1(b) is for a field normal to such a line ($M=\pm1$). In the latter case each solution is twice degenerate. Only OA modes are shown, the inactive modes being qualitatively similar, except the $M=0$ case looks like the OA, $M=\pm1$ modes, and vice versa. The separation parameter σ is in units of the sphere diameter so that unity means that the spheres touch. For large σ the modes approach the infinite sequence

$$\epsilon_l^{\infty}=-\frac{l+1}{l} \tag{35}$$

which are the poles of (34), or modes of the isolated sphere.[33] Each value of l gives rise to a different solution that remains distinct as the particles approach. We call these solutions the dipole mode ($l=1$), quadrupole mode ($l=2$), and so on. Only the lowest l-value curves are shown, as we have verified up to high values of l the rest to follow a qualitatively similar behavior. The variation

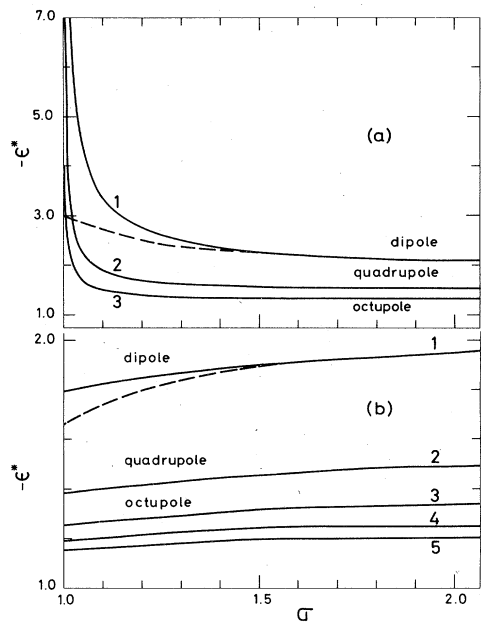


FIG. 1. Normal mode values of the particle dielectric constant as a function of the spacing parameter $\sigma=D/2a$. The first few OA modes are given for the two-sphere case (solid lines) for an exciting uniform external field parallel to the line joining the sphere centers (a), and perpendicular to this line (b). Dashed lines represent the dipole approximation and solid lines represent fully converged solutions. Integers label the electric multipole excited resonantly in each case.

with σ is monotonous and solutions diverge for $M=0$ as the spheres approach touching, whereas they decrease slowly in absolute value for $M=\pm 1$.

Dashed lines show in Fig. 1 solutions in the dipole, or $L=1$, approximation. Excitation of multipoles higher than the dipole are in these curves ignored. On the other hand, solid curves represent fully converged solutions. As expected from the short range of multipolar terms the dipole approximation is good for large separation but begins to fail at $\sigma\sim 1.5$. This failure is quite dramatic for parallel excitation ($M=0$) since the exact solutions diverge whereas the dipole approximation solution remains finite even for touching spheres. We have studied the convergence of the multipolar series as a function of σ for this case and our results are shown in Fig. 2 (solid curve). L^* is the multipole order that needs to be kept for the dipole mode solution to lie within 1% of the exact result. Thus for $\sigma=1.3$ up to quadrupole terms ($L^*=2$) are required, for $\sigma=1$ up to octupole terms ($L^*=3$), and so on. It is apparent from the figure that the number of terms needed in the perturbation series to achieve convergence diverges as the particles approach touching. Figure 2 gives a convenient convergence criterion valid even in more complex configurations of particles in two and three dimensions, as we shall see below. For perpendicular excitation ($M=\pm 1$) the effect on the position of the dipole resonance of couplings to multipoles of higher order than the dipole is small, the quadrupole approximation being sufficient for convergence even for touching spheres. We note however that in all cases convergence becomes slower for

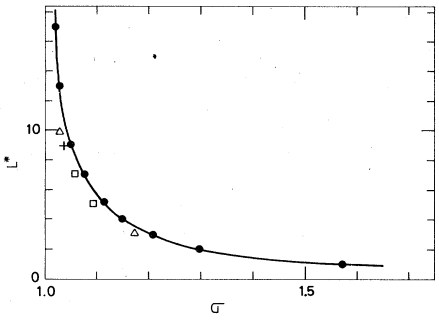


FIG. 2. Multipole order required in the perturbation series to reach within 1% from the exact value. Circles, triangles, squares, and cross are for the dipole mode resonance in the two sphere, linear chain, square lattice, and simple cubic lattice case, respectively.

higher order modes. For instance for touching spheres and perpendicular excitation convergence for the quadrupole mode as defined above requires $L^*=3$ (octupole approximation), and for the octupole mode, $L^*=5$ (2^5-pole approximation).

Because both particles acquire the same moments, in absolute value all modes are twice degenerate from the start. This symmetry is lost if a third particle is added at the same separation and aligned with the other two. As discussed in Sec. III the particle at the center is excited differently from the end particles so that now there will be two modes of exciting a dipole, quadrupole, or higher or-

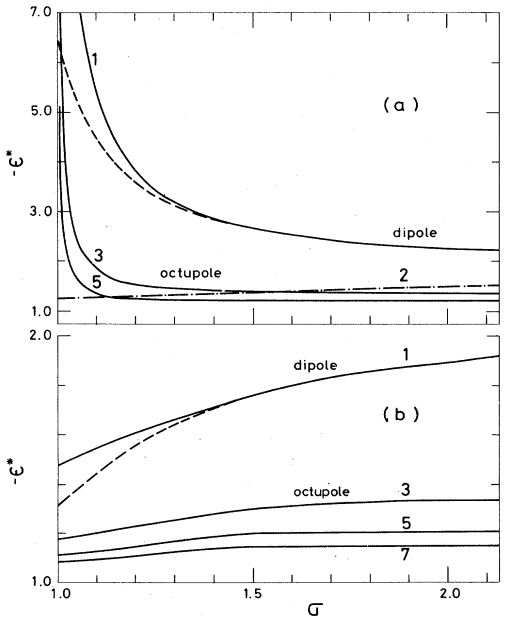


FIG. 3. Normal modes of the linear chain for an external field along the chain axis [$M=0$, case (a)], and perpendicular to it [$M=\pm 1$, case (b)]. The dashed-dotted line gives the only optically inactive mode shown here. Solid lines are fully converged solutions, and dashed lines are solutions in the dipole approximation. Integers label the electric multipole excited resonantly.

der resonance. Even in the dipole approximation, Eqs. (25) and (26) yield two solutions for the dipole modes:

$$-\epsilon^*_{\pm}=2\frac{(\pm\sqrt{513}-1)\sigma^3+4}{(\pm\sqrt{513}-1)\sigma^3-8}\ . \tag{36}$$

Our numerical studies of this case show that multipolar effects make all solutions diverge as the spheres approach touching. If more spheres are added along the line making an infinite string of equally spaced particles all of them are excited equally and the resonances have a similar behavior as in the $N=2$ case, as shown in Fig. 3. The main difference is that the quadrupole, 2^4-pole, and all even-order pole modes are missing due to symmetry-induced cancellations. In fact, an external uniform field does not excite even-order poles since there is no coupling between these and the odd-order ones. All even modes are thus inactive optically. We have included in Fig. 3(a) the quadrupole mode for the $M=0$ case (dashed-dotted line) and it is seen to be finite at all separations. In contrast, inactive modes for $M=\pm1$ are divergent. As before, solid lines represent fully converged solutions and dashed lines the dipole approximation. Convergence of solutions is a bit faster than for the $N=2$ case throughout the range of the separation parameter σ as is apparent in Fig. 2 (triangles), where we have included two representative points for the string. This is due to the absence of the coupling between the dipole and quadrupole or other even-order excitations due to symmetry.

Figure 4 shows our results for the infinite square lattice. Figure 4(a) is for the external field normal to the plane of the lattice ($M=0$) and Fig. 4(b) is for the field on the plane ($M=\pm1$). As for the infinite string, even and odd polarizations are not coupled and we only show the OA modes that are all of odd order. There is a coupling between different values of m for given l that was absent in the linear arrangements, however. For instance as expression (32) shows, q_{31} and q_{3-3} are coupled and the octupole resonance is thus split in two branches for $M=1$. Likewise, q_{50}, q_{5-4}, and q_{54} are coupled so the 5-pole resonance is split in three branches for $M=0$. As is apparent from Fig. 4, this splitting occurs when multipolar effects become important, at $\sigma\lesssim1.5$. For excitations perpendicular to the plane ($M=0$) the dipole and octupole modes are finite whereas the 5-pole mode has two finite and one divergent branch. Higher modes also have mixing of finite and diverging resonances yielding a very complex distribution of resonances for $\sigma<1.6$, where multipole crossings occur. The dashed-dotted line in Fig. 4(a) represents a resonance whose nature is not well understood at the present. It appeared at all approximations as the lowest solution in $-\epsilon^*$, but in the next-order solution this resonance was pushed upwards, the resonance being now assumed by the lowest solution of this higher-order result. For a field on the plane all resonances diverge and there are no crossing as shown in Fig. 4(b). Convergence in this case is the same as for the linear chain as suggested by the two representative points included in Fig. 2 (squares). A similar situation occurs in the simple cubic lattice configuration, as can be seen from Fig. 5 and the representative point in Fig. 2 (cross).

The above examples show that the dipole approxima-

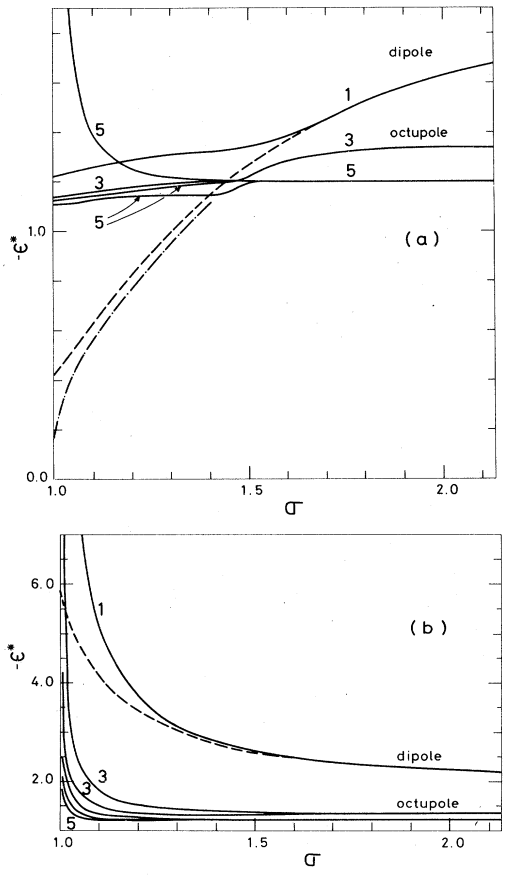


FIG. 4. Normal modes of the square lattice for an external field normal to the plane of the lattice [$M=0$, case (a)], and on the plane [$M=\pm1$, case (b)]. Solid lines are fully converged solutions and dashed lines, solutions in the dipole approximation. The dashed-dotted line is explained in the text. Integers label the electric multipole excited resonantly.

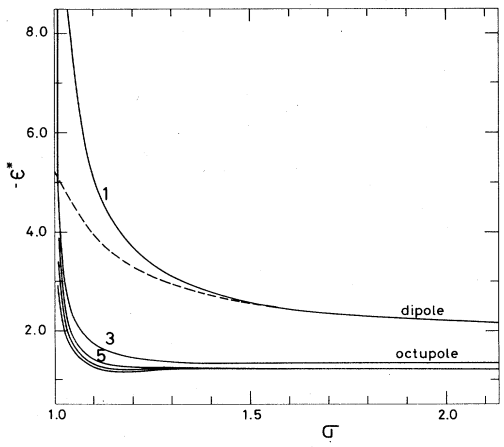


FIG. 5. Normal modes of the cubic lattice for an external field along one of the principal axes ($M=0$). Solid lines are fully converged solution, and dashed lines are solutions in the dipole approximation. Integers label the electric multipoles excited resonantly.

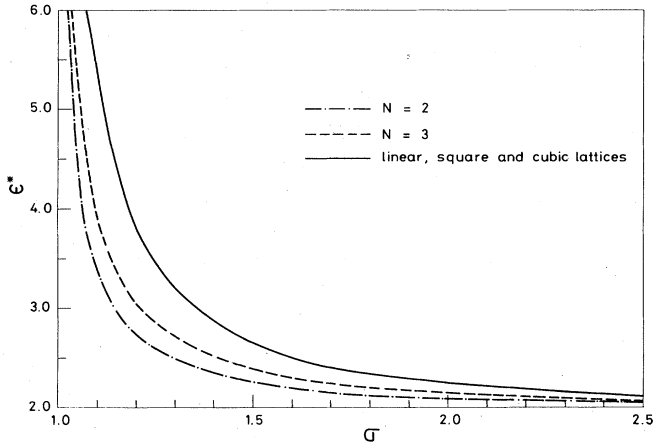


FIG. 6. Diverging OA dipole resonance for two spheres (dashed-dotted line), three aligned spheres (dashed line), and linear, square, and cubic lattices (solid line).

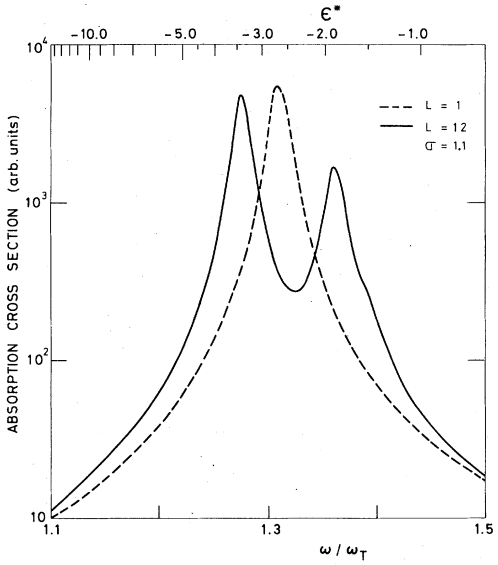


FIG. 7. Absorption spectrum for two equal NaCl spheres separated by 1.1 diameters and excited with a field along the line joining their centers. The solid line includes multipoles up to order $L=12$, and the dashed line is the dipole approximation.

tion fails not only because it yields just one resonance but also because this resonance is in the wrong place in all cases for $\sigma \lesssim 1.5$. It may be used safely, however, in obtaining the dipole resonance for an interparticle separation greater than three particle radii, except for the square lattice and an external field normal to the plane, in which case the region $1.5 \lesssim \sigma < 1.7$ is strongly affected by the proximity of the dipole to other modes, and in which case the region of applicability is $\sigma \gtrsim 1.7$. Our results also show striking similarities for arrangements of particles in one, two, and three dimensions as is apparent in Figs. 1(a), 3(a), 4(b), and 5. One may understand these similarities by noting that in all the cases cited the external field has a component along the axis joining two nearest-neighbor spheres. The multipolar interaction is short range and its effect is dominated by the nearest-neighbor couplings so that the $N=2$ results are reproduced in essence in all the cases mentioned. There is a difference in strength in the coupling however, as is apparent in Fig. 6 where we have drawn together the diverging dipole resonances. As more particles are added along the field direction the dipole local field increases, pushing the resonance further away from the isolated sphere value of $\epsilon^* = -2$. In infinite arrangements the linear chain configuration dominates over lateral interactions and the square and cubic lattices give results that are indistinguishable from the linear chain in the scale of the figure. We conclude that dimensionality is not an important consideration in determining the position of the dipole resonance for excitation along an infinite dimension. The octupole and higher resonances also coincide in this case, save for the splitting near $\sigma=1.0$ caused by couplings between neighbor strings in the square and cubic lattices. Dimensionality does play a role for excitation along a dimension that is empty as Figs. 3(b) and 4(a) show, the main difference between these being that in the latter case there are resonances that diverge which do not in the former. These resonances are weak, however, and they do not play an important role in the optical spectrum of the system.

The absorption cross section was also computed using Eq. (18) and NaCl as a test system. For this material the usual dispersion relation was used[34] with the optical parameters[35] $\epsilon_0=5.934$, $\epsilon_\infty=2.328$, $\omega_T=164$ cm^{-1}, and $\gamma=0.02\omega_T$. Figure 7 shows for $N=2$ and $\sigma=1.1$ how the dipole approximation fails when the particles are too close. In the fully converged calculation (solid line) the dipole resonance is shifted towards the infrared and a new resonance appears arising mainly from the excitation of the quadrupole mode. As the spheres are drawn closer together higher pole modes are excited resonantly, as shown in Fig. 8. For $\sigma=1.02$, strong quadrupole and octupole

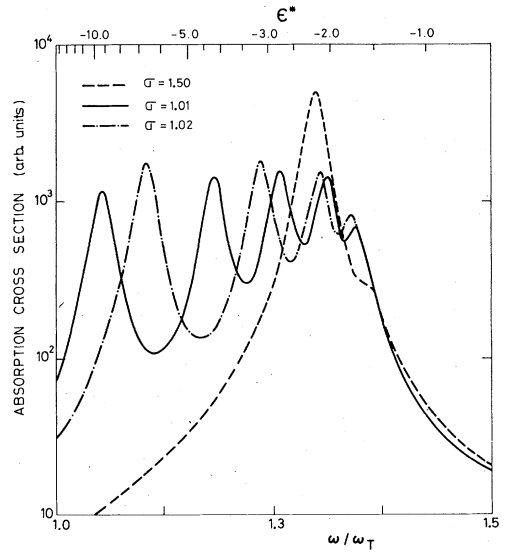


FIG. 8. Absorption spectrum for two equal NaCl spheres at separations $\sigma=1.50$ (dashed line), $\sigma=1.02$ (dashed-dotted line), and $\sigma=1.01$ (solid line).

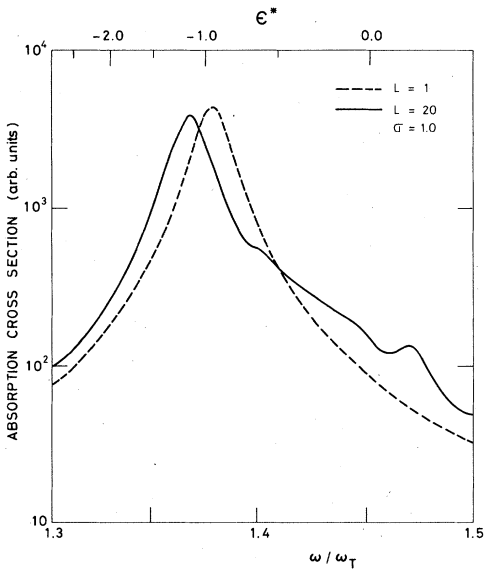


FIG. 9. Absorption spectrum for two equal NaCl spheres that touch and an external field normal to the line joining the centers.

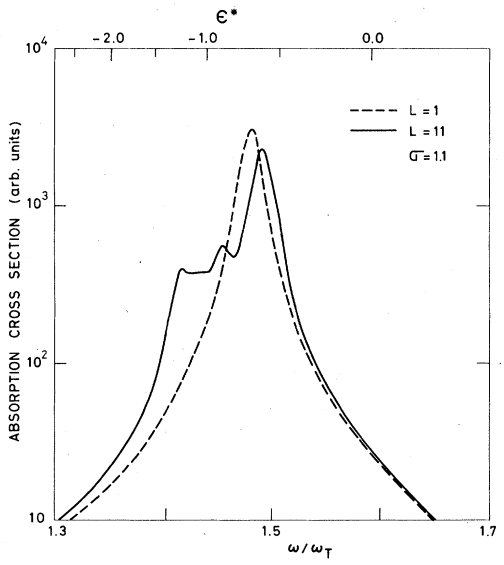


FIG. 10. Absorption spectrum for a square lattice of NaCl spheres excited by a field normal to the plane of the lattice. The lattice constant is $\sigma = 1.1$.

peaks are added to the dipole resonance and a weak maximum reveals the onset of the 2^4-pole resonance. For $\sigma = 1.01$ all resonances are shifted to the infrared, the 2^4-pole becomes strong, and the 2^5-pole resonance appears at the high-frequency edge of the spectrum. Note the shift of the left edge towards smaller frequencies while the right edge essentially does not move. Note also that for such a small change in σ of less than 1% the spectrum changes qualitatively, showing how sensitive it is to particle separation. All curves in Fig. 8 were obtained with $L = 40$ and were checked for full convergence. When the spheres touch, Fig. 1(a) indicates that all resonances lie at $\epsilon^* = -\infty$ which is the bulk resonance at frequency ω_T. Because the multipolar series solution is not convenient for checking this assertion numerically, it remains as a conjecture suggested by our results. The multipolar shift towards the infrared is well established by our calculations, however, and is consistent with the experimental evidence.[5,8,15,36] The cases $N = \infty$ and $M = 0$, square lattice and $M = 1$, and cubic lattice, $M = 0$, showed the same qualitative behavior as described above and will not be discussed here further.

Figures 9 and 10 show the effect of multipolar couplings on solutions that do not diverge. Figure 9 is for $N = 2$ and $M = 1$ and Fig. 10 for the square lattice and an external field normal to the plane ($M = 0$). The dipole resonance is somewhat shifted by the couplings and higher pole modes induce some structure to a wing of the resonance. The effect, although noticeable, is rather weak. It is interesting that in the square-lattice case the strongest peak is not the direct dipole mode. By this we mean that the lowest curve in the left-hand side of Fig. 4(a) to which the peak corresponds may not be connected by continuity to the $\epsilon^* = -2$ as the spheres are drawn apart. The peak is reminiscent of the dipole resonance, however, because of its relative strength and since it appeared as a continuous evolution of the dipole resonance obtained in the dipole approximation as it was made better by inclusion of higher multipoles, one at a time.

V. SUMMARY AND CONCLUSIONS

We have presented a theory of static electromagnetic modes in particulate matter that yields expressions for the resonances simple enough to include high-order multipoles in actual computations. We were then allowed to reach full multipolar convergence in obtaining the resonances and thus to assess the importance of multipolar effects in various cases involving dielectric spheres. Our main findings are that the normal modes are infinite in number, yielding a structure on the absorption spectrum, and that the dipole approximation fails in all cases when the interparticle distance is less than three particle radii. These results were anticipated in previous work involving two spheres.[4,5] The number of multipolar terms needed for convergence in optically active modes diverges as the spheres approach touching if the external field is along a direction where two or more particles lie in line. The resonance value of the dielectric constant itself diverges so that the bulk resonance is approached by all modes. This is clearly seen in the absorption curves for particles made of an ionic material such as NaCl for which we have shown how sensitive the peak positions are to interparticle separation, all moving towards the bulk resonance in the infrared as the particles approach touching. This suggests that the peak positions provide an accurate measurement of the distance between particles in configurations where this distance is well defined, such a single pair or a perfect lattice. Disorder on the other hand would readily destroy the structure in the absorption spectrum. For an external field normal to the axis of a one dimensional arrangement, or normal to the plane for a square lattice, the pattern of

resonances depends much on the geometry. There may be purely finite solutions or a combination of diverging and finite resonances. The absorption spectrum consists of a main resonance with some wing structure whose detail depends on the diversity referred to above. Multipolar effects appear not as dramatic for this perpendicular excitation as for axial excitation. Modes that are optically inactive display similar patterns as OA modes and may be obtained with the same convergence criterion described above and will not be discussed here. They have no effect in optical absorption but are relevant in dynamic couplings such as those that arise in van der Waals forces.[27,28] Finally, the effect of dimensionality is found to be unimportant for axial excitation suggesting that the important couplings occur in this case between neighbors along the axis only. For perpendicular excitation in the linear and planar cases dimensional effects arise that have a weak bearing in the optical spectrum.

ACKNOWLEDGMENTS

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APPENDIX

We derive an alternative expression for the sum (12). Consider the set of linear equations for the unknowns x_μ

$$x_\mu=\delta_{\mu\bar{\mu}}f+\sum_{\mu'}B_\mu^{\mu'}x_{\mu'}\ , \tag{A1}$$

where μ is a set of indices. If we separate from the sum the term proportional to x_μ and iterate over the remainder indefinitely, we obtain the solution

$$x_\mu=\delta_{\mu\bar{\mu}}f+\frac{Q_\mu^{\bar{\mu}}}{1-Q_\mu^\mu}f\ , \tag{A2}$$

where Q is defined as in (12). The above expression is just a special case of (11), with a simple nonzero component for F_μ. An alternative solution to (A1) is obtained by direct use of Kramer's rule,

$$x_\mu=-\frac{\mathrm{cof}(B_{\bar{\mu}}^\mu-\delta_{\mu\bar{\mu}})}{\det(\underline{B}-\underline{I})}f\ . \tag{A3}$$

Here the matrix $\underline{B}$ has components B_α^β. Comparing (A2) and (A3) for the case $\bar{\mu}=\mu$ we obtain

$$Q_\mu^\mu=1+\frac{\det(\underline{B}-\underline{I})}{\mathrm{cof}(B_\mu^\mu-1)}\ . \tag{A4}$$

Doing the same for $\mu\neq\bar{\mu}$ yields

$$Q_\mu^{\bar{\mu}}=-(1-Q_\mu^\mu)\frac{\mathrm{cof}B_{\bar{\mu}}^\mu}{\det(\underline{B}-\underline{I})}\ ,$$

which after use of (A4) becomes

$$Q_\mu^{\bar{\mu}}=\frac{\mathrm{cof}(B_{\bar{\mu}}^\mu)}{\mathrm{cof}(B_\mu^\mu-1)}\ . \tag{A5}$$

From the properties of determinants it follows that this last expression may be written in identical form as (A4) with the prescription that in the μth column of the determinant one must replace B_α^μ by $B_\alpha^{\bar{\mu}}$. The formulas just derived are extremely useful since they turn an infinite sum into a simple combination of determinants the order of which is at most the range of μ.

There is still another way to express the sum. Suppose $\mu=(\lambda,i)$ where λ and i run over independent set of integers. For instance we could have $\lambda=(l,m)$, and i, the particle label. We can then iterate (A1) in a different form. We first separate from the sum the terms with $\lambda'=\lambda$, that is, we write

$$x_{\lambda i}=\delta_{\lambda\bar{\lambda}}\delta_{i\bar{i}}f+\sum_{i'}B_{\lambda i}^{\lambda i'}x_{\lambda i'}+\sum_{\lambda',i'}{}'B_{\lambda i}^{\lambda' i'}x_{\lambda' i'}\ ,$$

where the prime in the sum means that $\lambda'=\lambda$ is to be excluded from the summation, i' remaining unrestricted. Iterating on the remaining sum indefinitely, always separating terms containing $x_{\lambda i'}$ one obtains

$$x_{\lambda i}=g_{\lambda i}+\sum_{i'}P_{\lambda i}^{\lambda i'}x_{\lambda i'}\ , \tag{A6}$$

where

$$\begin{aligned}g_{\lambda i}&=\delta_{\lambda\bar{\lambda}}\delta_{i\bar{i}}f+(1-\delta_{\lambda\bar{\lambda}})P_{\lambda i}^{\bar{\lambda}\bar{i}}f\ ,\\ P_{\lambda i}^{\bar{\lambda}\bar{i}}&=B_{\lambda i}^{\bar{\lambda}\bar{i}}+\sum_{\lambda',i'}{}'B_{\lambda i}^{\lambda' i'}B_{\lambda' i'}^{\bar{\lambda}\bar{i}}\\ &\quad+\sum_{\substack{\lambda',i',\\ \lambda'',i''}}{}'B_{\lambda i}^{\lambda' i'}B_{\lambda' i'}^{\lambda'' i''}B_{\lambda'' i''}^{\bar{\lambda}\bar{i}}+\cdots\ .\end{aligned} \tag{A7}$$

Note that $P_{\lambda i}^{\bar{\lambda}\bar{i}}$ contains all possible couplings of (λ,i) to $(\bar{\lambda},\bar{i})$ through members of the set not involving λ. $Q_{\lambda i}^{\bar{\lambda}\bar{i}}$ is more inclusive since it only leaves λ out when i is involved. Repeated iteration of (A6) retaining each time the term with $x_{\lambda i}$ yields

$$x_{\lambda i}=g_{\lambda i}+\sum_{i'(\neq i)}Q_{\lambda i}^{\lambda i'}g_{\lambda i'}+Q_{\lambda i}^{\lambda i}x_{\lambda i}\ , \tag{A8}$$

which is of the same form as (11). Here, however,

$$\begin{aligned}Q_{\lambda i}^{\bar{\lambda}\bar{i}}&=P_{\lambda i}^{\bar{\lambda}\bar{i}}+\sum_{i'(\neq i)}P_{\lambda i}^{\lambda i'}P_{\lambda i'}^{\bar{\lambda}\bar{i}}\\ &\quad+\sum_{\substack{i'(\neq i),\\ i''(\neq i)}}P_{\lambda i}^{\lambda i'}P_{\lambda i'}^{\lambda i''}P_{\lambda i''}^{\bar{\lambda}\bar{i}}+\cdots\ .\end{aligned} \tag{A9}$$

That this sum, as suggested by the notation, is the same as (12), can be seen if we write (A8) for $\lambda\neq\bar{\lambda}$, $i\neq\bar{i}$. Then $g_{\lambda i}=P_{\lambda i}^{\bar{\lambda}\bar{i}}f$, and we have

$$x_{\lambda i}=\left[P_{\lambda i}^{\bar{\lambda}\bar{i}}+\sum_{i'(\neq i)}Q_{\lambda i}^{\lambda i'}P_{\lambda i'}^{\bar{\lambda}\bar{i}}\right]f+Q_{\lambda i}^{\lambda i}x_{\lambda i}\ . \tag{A10}$$

Using (A7) and (A9) one may easily check that the parentheses equals $Q_{\lambda_i}^{\bar{\lambda}\bar{i}}$. Comparison with (A2) then shows the desired equivalence. One may use (A4) and

(A5) to sum (A9). The result is

$$Q_{\lambda i}^{\bar{\lambda}\bar{i}}=1+\frac{\det(\bar{\underline{P}}-\underline{I})}{\mathrm{cof}(P_{\lambda i}^{\lambda i}-1)}\ , \tag{A11}$$

where the matrix in the denominator has elements $P_{\lambda j}^{\lambda j'}$ and in the numerator $\bar{\underline{P}}$ differs from such matrix in that in the ith column $P_{\lambda j}^{\lambda i}$ must be replaced by $P_{\lambda j}^{\bar{\lambda}\bar{i}}$.

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