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Local-Field Corrections to Coulomb Interactions

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The effective charge-charge, charge-dipole, and dipole-dipole Coulomb interactions are calculated for a solid dielectric. The static dielectric screening of the solid is included by using the point-dipole model, which assumes that the host ions are polarizable points. This model allows the dielectric screening of Coulomb interactions to be included exactly, since the local-field corrections can be summed to all orders. The long-range charge-charge interactions are just screened by ϵ^{-1}, where ϵ is the Lorentz-Lorentz dielectric function. The long-range interactions involving dipoles can be understood by assigning the dipoles an external moment $\mu_e=(\epsilon+2)\mu/3$, where μ is the moment in a vacuum. This form of the external moment applies only to dipoles in positions of cubic symmetry.

I. INTRODUCTION

In a vacuum, the Coulomb interaction between two charges q_1 and q_2 is q_1q_2/R, where R is their separation. In an appropriately homogeneous, isotropic material with dielectric constant ϵ, the interaction is $q_1q_2/\epsilon R$. Similarly, the charge-dipole and dipole-dipole interactions in vaccum are

$$V_{\mathrm{cd}}=+q\boldsymbol{\mu}\cdot\mathbf{R}/R^3\,, \tag{1}$$

$$V_{\mathrm{dd}}=\boldsymbol{\mu}_1\cdot\boldsymbol{\phi}(\mathbf{R})\cdot\boldsymbol{\mu}_2\,, \tag{2}$$

where

$$\boldsymbol{\phi}(\mathbf{R})=(\mathbf{I}-3\hat{R}\hat{R})/R^3\,. \tag{3}$$

The question of interest here is the change in these interactions in a solid with dielectric constant ϵ.

The reason that the charge-charge interaction is reduced by ϵ^{-1} in the dielectric is that the host ions in the solid are polarizable. They polarize around the impurity charges q_1 and q_2, which reduces the effective interaction between q_1 and q_2. Viewed microscopically, if one knows the position of all the host ions, and their polarizability, the effective screening can be evaluated from first principles. This is done below for the charge-charge interaction in cubic crystals, and the effective interaction at large R is just reduced by ϵ^{-1}. The same method of summing the local-field corrections is then applied to the charge-dipole and dipole-dipole interactions. In the limit of large separation, the local-field corrections to these interactions can also be expressed simply in terms of the static dielectric constant. These results are summarized in Table I. It is shown that for interstitial impurities, the long-range dipole interactions can be characterized by assigning the dipole an external moment[1–3] $\boldsymbol{\mu}_e=(\epsilon+2)\boldsymbol{\mu}/3$, where $\boldsymbol{\mu}$ is the moment in a vacuum. The moments $\boldsymbol{\mu}$ are viewed as rigid, and their magnitude is not altered by electric fields. The increase of $\boldsymbol{\mu}_e$ over $\boldsymbol{\mu}$ arises from the polarization of the ions surrounding the impurity moment.

TABLE I. The long-range Coulomb interactions in cubic dielectrics. For dipoles at interstitial, yet cubic, symmetry sites, the dipole interactions can be expressed in terms of an external moment $\boldsymbol{\mu}_e=(\epsilon+2)\boldsymbol{\mu}/3$. The enhancement of the moment derives from the Lorentz internal-field corrections. The dipole-dipole interaction is $\boldsymbol{\phi}=(\mathbf{I}-3\hat{R}\hat{R})R^{-3}$.

	Vacuum	Cubic dielectric	External moment
charge-charge	q_1q_2/R	$q_1q_2/\epsilon R$	
charge-dipole	$q=\boldsymbol{\mu}\cdot\mathbf{R}/R^3$	$\dfrac{\epsilon+2}{3\epsilon}q\boldsymbol{\mu}\cdot\mathbf{R}/R^3$	$q\boldsymbol{\mu}_e\cdot\mathbf{R}/\epsilon R^3$
dipole-dipole	$\boldsymbol{\mu}_1\cdot\boldsymbol{\phi}\cdot\boldsymbol{\mu}_2$	$\left(\dfrac{\epsilon+2}{3}\right)^2\dfrac{\boldsymbol{\mu}_1\cdot\boldsymbol{\phi}\cdot\boldsymbol{\mu}_2}{\epsilon}$	$\boldsymbol{\mu}_{1e}\cdot\boldsymbol{\phi}\cdot\boldsymbol{\mu}_{2e}/\epsilon$

My interest in the local-field corrections to dipole-dipole interactions was stimulated by recent dielectric measurement of OH$^-$ molecules in KCl by Känzig, Hart, and Roberts.[4] The theoretical calculations[5–8] on these systems can only agree with experiment by assuming a dipole moment which is twice as large as that observed. Klein[6] used (2) divided by ϵ for his dipole-dipole interactions. Lawless[7] used local-field corrections based on Fröhlich's models.[2] In Sec. IV it is shown that the correct enhancement factor for long-range dipole-dipole interactions is

$$\left(\frac{\epsilon+2}{3}\right)^2\frac{1}{\epsilon}(\boldsymbol{\mu}'/\mu)^2. \tag{4}$$

The factor $\boldsymbol{\mu}'/\mu$, defined in Eq. (27), arises because the impurities are at substitutional sites. It is due to the change in the dielectric properties of the medium caused

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[1] L. Onsager, J. Am. Chem. Soc. 58, 1486 (1936).

[2] H. Frohlich, *Theory of Dielectrics* (Clarendon Press, Oxford, England, 1958).

[3] Onsager (Ref. 1) defines the external moment as that which "determines the force . . . which the dipole will exert upon a distant charge in the dielectric".

[4] W. Känzig, H. R. Hart, Jr., and S. Roberts, Phys. Rev. Letters 13, 543 (1964).

[5] W. Zernik, Phys. Rev. 139, A1010 (1965).

[6] M. W. Klein, Phys. Rev. 141, 489 (1966).

[7] W. N. Lawless, Phys. Cond. Mat. 5, 100 (1966).

[8] M. E. Baur and W. R. Salzman, Phys. Rev. Letters 16, 701 (1966).

by the absence of a host polarizable ion. The ratio $\mathbf{\mu}'/\mu$ depends upon ϵ, but the functional form of this ϵ dependence cannot be reduced to a simple analytical form.

Since the static dielectric constant in KCl is[4] $\epsilon_0=4.4$, the enhancement factor is $1.03(\mathbf{\mu}'/\mu)^2$, which is negligible for $\mathbf{\mu}'\approx\mu$. The external moment is 2.1 μ, which justifies Klein's use of 2 μ in his calculations. But at the peak of the dielectric-constant data, $\epsilon\sim10$, which gives an enhancement of 1.6 $(\mathbf{\mu}'/\mu)^2$ to the dipole-dipole interactions. The paraelectric polarizability of the impurity dipoles, which contributes to ϵ, therefore enhances the interaction between any two impurity dipoles. The moment entering into the formula for ϵ also contains μ_e, and thus depends upon ϵ.

The statement that the paraelectric contributions to ϵ affect the strength of the dipole-dipole interactions makes the external moment depend upon temperature, impurity concentration, and applied electric field. This statement assumes that the results for cubic arrays also apply to random arrays. This is reasonable since the average field from a random array is that of a uniform array, which is essentially cubic. This could explain the observation of Bron and Dreyfus[9] that the effective dipole moment appeared to depend upon the concentration of impurities. A similar experiment by Feher, Shepherd, and Shore[10] did not have this difficulty, and the value of the OH^- moment they report is in agreement with Kuhn and Luty.[11] Since the experiment of Feher *et al.* was done at much lower OH^- concentration, one would not expect a significant contribution to the external moment in their case. This could explain some of the discrepancy between these two experiments. We also note that in an earlier adiabatic depolarization experiment by Shepherd and Feher,[12] they reported a higher value of the moment in more concentrated systems.

The local-field corrections are summed microscopically, assuming that the induced moments on the host ions are point dipoles. This convenient model allows the general formulas to be expressed in compact form. The method used to sum the local fields has been used recently in the discussion of van der Waal's forces in solids.[13–17] The final formulas are given only for cubic lattices, since they are particularly simple in this case.

II. CHARGE-CHARGE

The two charges q_1 and q_2 are in a host lattice at points $\mathbf{l}_1$ and $\mathbf{l}_2$. It is convenient to assume that they are at interstitial positions, so as not to disturb the dielectric properties of the host lattice. The simple extension to substitutional impurities is given at the end. The host ions are at lattice sites $\mathbf{l}_j$, and each has an induced moment $\mathbf{P}_j$ whose amplitude is proportional to q_1 and q_2. The Hamiltonian is

$$\mathcal{H}=\frac{q_1q_2}{l_{12}}+q_1\sum_j \mathbf{P}_j\cdot\frac{\mathbf{l}_{j1}}{l_{j1}^3}+q_2\sum_j\frac{\mathbf{P}_j\cdot\mathbf{l}_{j2}}{l_{j2}^3}+\tfrac{1}{2}\sum_{jj'}\mathbf{P}_j\cdot\boldsymbol{\phi}_{jj'}\cdot\mathbf{P}_j,$$

where $\mathbf{l}_{j1}=\mathbf{l}_j-\mathbf{l}_1$, and $\boldsymbol{\phi}_{ij}=\boldsymbol{\phi}(\mathbf{l}_i-\mathbf{l}_j)$ is the dipole-dipole interaction (3).

This Hamiltonian leads to four types of energy terms. One is just the van der Waal's binding energy of the solid, which is independent of q_1 and q_2. The second term depends upon q_1^2 and the third upon q_2^2. These two are just the energy needed to put the separate charges into the polarizable medium, and they are independent of the position within the lattice. The fourth term is proportional to q_1q_2 and depends explicitly upon the separation of $\mathbf{l}_1$ and $\mathbf{l}_2$. This last term we call the "effective interaction," although a more conventional name for this section would be the "screened Coulomb interaction." The evaluation of this effective interaction gives the local-field corrections to the Coulomb interactions. The superposition principle shows that these four energy terms are independent.

The effective interaction between q_1 and q_2 is obtained by eliminating the induced moments $\mathbf{P}_j$ from the equation. Because of the superposition principle, which is just an assumption of linear polarization response to an electric field, only the terms in $\mathbf{P}_j$ which are caused by q_1 and q_2 need to be considered. One can see the types of terms which occur by noting that the electric field at a site $\mathbf{l}_j$ is

$$E_j=-\frac{q_1\mathbf{l}_{j1}}{l_{j1}^3}-\frac{q_2\mathbf{l}_{j2}}{l_{j2}^3}-\sum_{j'}\boldsymbol{\phi}_{jj'}\cdot\mathbf{P}_{j'} \tag{5}$$

and using the definition of ion polarizability $\boldsymbol{\alpha}_j$,

$$\mathbf{P}_j=V_0\boldsymbol{\alpha}_j\cdot\mathbf{E}_j,$$

where V_0 is the volume per host ion. However, if one evaluates $\mathbf{P}_j$ by this method, and inserts the result in $\mathcal{H}$, one miscounts the number of times each interaction occurs.

The effective interaction is correctly given by the series

$$V_{cc}=q_1q_2\Bigg[\frac{1}{l_{12}}-V_0\sum_j\frac{\mathbf{l}_{1j}\cdot\boldsymbol{\alpha}_j\cdot\mathbf{l}_{2j}}{l_{1j}^3l_{2j}^3}+V_0^2\sum_{ij}\frac{\mathbf{l}_{1j}\cdot\boldsymbol{\alpha}_j\cdot\boldsymbol{\phi}_{ji}\cdot\boldsymbol{\alpha}_i\cdot\mathbf{l}_{2i}}{l_{1j}^3l_{2i}^3} -V_0^3\sum_{ijk}\mathbf{l}_{1j}\cdot\boldsymbol{\alpha}_j\cdot\boldsymbol{\phi}_{ji}\cdot\boldsymbol{\alpha}_i\cdot\boldsymbol{\phi}_{ik}\cdot\boldsymbol{\alpha}_k\cdot\mathbf{l}_{k2}/l_{2k}^3l_{1j}^3+\cdots\Bigg]. \tag{6}$$

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[9] W. E. Bron and R. W. Dreyfus, Phys. Rev. Letters **16**, 165 (1966).

[10] G. Feher, I. W. Shepherd, and H. B. Shore, Phys. Rev. Letters **16**, 500 (1966).

[11] U. Kuhn and F. Luty, Solid State Commun. **2**, 281 (1964); **4**, 31 (1965).

[12] I. Shepherd and G. Feher, Phys. Rev. Letters **15**, 194 (1965).

[13] S. Doniach, Phil. Mag. **8**, 129 (1963).

[14] A. D. McLachlan, R. D. Gregory, and M. A. Ball, Mol. Phys. **7**, 119 (1964).

[15] A. Lucas, Phys. Letters **12**, 325 (1964).

[16] A. Lucas, thesis, Université de Liege, 1966 (unpublished).

[17] G. D. Mahan, J. Chem. Phys. **43**, 1569 (1965).

The correct counting is achieved by expanding the free energy[18,19]

$$F=-\beta^{-1}\ln\left\langle\exp\left[-\int_0^\beta d\tau\,\mathcal{H}(\tau)\right]\right\rangle$$

and sorting out its diagrams. Irreducible (connected) diagrams which are independent of q_1 and q_2 give the van der Waals binding energy. Clusters which start and end at the same charge (q_1 or q_2) contribute to the polarization self-energy of that charge. The effective interaction is found from clusters which start at one charge and end on the other. Thus, this method generates all four of the energy terms mentioned above. The polarizability is introduced into these clusters by requiring that the only nonzero contractions are

$$\int_0^\beta d\tau\,\langle T_\tau \mathbf{P}_j(\tau)\mathbf{P}_{j'}(\tau')\rangle=V_0\alpha_j\delta_{jj'}\,,$$

where T_τ is the usual tau ordering operator.[19] In this formalism, the polarizability $\alpha(\omega)$ is a thermodynamic Green's function[19] which is evaluated only at zero frequency. One advantage of this formalism is that it gives a rigorous method of extending (6) to finite frequencies and to finite temperatures.

The infinite series of terms in the equation for V_{cc} can be summed exactly. This is done by changing the sums over $\mathbf{l}_j$ to wave-vector sums. For simplicity, we assume that the ions are identical, and $\boldsymbol{\alpha}$ is independent of j. Define[17]

$$\mathbf{T}(\mathbf{k})=\frac{V_0}{4\pi}\sum_{\mathbf{l}\neq 0}\exp[i\mathbf{k}\cdot\mathbf{l}]\boldsymbol{\phi}(\mathbf{l})\,, \tag{7}$$

$$\mathbf{W}(\mathbf{k})=V_0/4\pi\sum_{\mathbf{l}}e^{i\mathbf{k}\cdot(\mathbf{l}-\mathbf{l}_0)}(\mathbf{l}-\mathbf{l}_0)/|\mathbf{l}-\mathbf{l}_0|^3\,, \tag{8}$$

$$\mathbf{R}(k)=4\pi\boldsymbol{\alpha}\cdot\mathbf{T}(\mathbf{k})\,.$$

The $\mathbf{l}$ sums are over lattice sites, while $\mathbf{l}_0$ is the vector from the interstitial impurity to a lattice site. The equation for V_{cc} is now

$$\begin{aligned}V_{cc}=\frac{q_1q_2}{l_{12}}-q_1q_2\frac{4\pi}{V}\sum_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{l}_{21}}[&4\pi\mathbf{W}(\mathbf{k})\cdot\boldsymbol{\alpha}\cdot\mathbf{W}(-\mathbf{k})\\&-4\pi\mathbf{W}(k)\cdot\mathbf{R}(k)\cdot\boldsymbol{\alpha}\cdot\mathbf{W}(-\mathbf{k})\\&+4\pi\mathbf{W}\cdot\mathbf{R}\cdot\mathbf{R}\cdot\boldsymbol{\alpha}\cdot\mathbf{W}+\cdots]\,.\end{aligned} \tag{9}$$

To conform with Doniach's notation,[13] define

$$\mathbf{G}=\mathbf{I}-\mathbf{R}+\mathbf{R}\cdot\mathbf{R}-\cdots=[\mathbf{I}+\mathbf{R}]^{-1}\,, \tag{10a}$$

or

$$[\mathbf{I}+\mathbf{R}]\cdot\mathbf{G}=\mathbf{I}\,. \tag{10b}$$

Then the infinite sum becomes

$$V_{cc}=\frac{q_1q_2}{l_{12}}-q_1q_2\frac{4\pi}{V}\sum_{k}e^{i\mathbf{k}\cdot\mathbf{l}_{21}}4\pi\mathbf{W}(\mathbf{k})\cdot\boldsymbol{\alpha}\cdot\mathbf{G}(\mathbf{k})\cdot\mathbf{W}(-\mathbf{k})\,. \tag{11}$$

This result is true for a lattice of arbitrary symmetry. But it is convenient to specialize to cubic lattices where the polarizability is isotropic, $\boldsymbol{\alpha}=\alpha\mathbf{I}$. Cubic crystals also have the property that the matrix $\mathbf{T}(\mathbf{k})$ is diagonal in the coordinate system defined by the three orthonormal unit vectors $\hat{k}=\hat{e}_3$, $\hat{e}_1$, and $\hat{e}_2$,

$$\hat{e}_i\cdot\mathbf{T}(\mathbf{k})\cdot\hat{e}_j=\delta_{ij}T_i(\mathbf{k})\,. \tag{12}$$

This allows $\mathbf{G}(\mathbf{k})$ in (10) to be expressed as

$$\mathbf{G}(\mathbf{k})=\sum_{i=1}^{3}\frac{\hat{e}_i\hat{e}_i}{1+4\pi\alpha T_i(\mathbf{k})}\,. \tag{13}$$

This simple form of $\mathbf{G}$ is only valid for cubic lattices. But the equivalent solution for other lattice symmetries is easily obtained by finding the most general form of $\mathbf{R}$ from group theory, and then inverting the matrix equation (10b). The matrix $\mathbf{G}$ is simply related to the dielectric tensor.

The prescription for finding the effective interaction between two charges is to evaluate $\mathbf{W}(\mathbf{k})$ and $\mathbf{T}(\mathbf{k})$ and then do the wave vector sums[20] over the Brillouin zone in (11). For $\mathbf{l}_{12}$ small, of the order of a lattice constant, this effort is necessary. But for $\mathbf{l}_{12}$ large, only small values of $\mathbf{k}$ in the sum should be important, and we can expand $\mathbf{W}$ and $\mathbf{T}$ around their $\mathbf{k}=0$ values:[21]

$$\begin{aligned}&\lim_{k\to0}\mathbf{W}(\mathbf{k})=i\mathbf{k}/k^2\,,\\&\lim_{k\to0}T_j(\mathbf{k})=-\tfrac{1}{3},\ j=1,2\\&\qquad\qquad\quad=\tfrac{2}{3},\ j=3\,.\end{aligned}$$

Since $\mathbf{W}$ is in the direction $\mathbf{k}$, only the T_3 component enters the $\mathbf{k}$ sum in (11). For large l_{12}

$$V_{cc}(\mathbf{l}_{12})\xrightarrow[l_{12}\to\infty]{}q_1q_2\left[\frac{1}{l_{12}}-\frac{4\pi\alpha}{1+8\pi\alpha/3}\frac{4\pi}{V}\sum_{k}\frac{e^{i\mathbf{k}\cdot\mathbf{l}_{12}}}{k^2}\right],$$

we approximate

$$\frac{4\pi}{V}\sum_{k}\frac{e^{i\mathbf{k}\cdot\mathbf{l}_{12}}}{k^2}\simeq\frac{1}{l_{12}}\,. \tag{14}$$

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[18] R. Brout and P. Carruthers, *Lectures on the Many-Electron Problems* (Interscience Publishers, Inc., New York, 1963).

[19] A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[20] It has recently become apparent that it is necessary to do these wave-vector sums in order to obtain accurate numerical answers for local-field corrections. This is shown in Ref. 16.

[21] This method has its dangers. By using the $k\to0$ limit for $\epsilon(k)$ in an electron gas, one misses the Friedel oscillations. It is conceivable that similar effects are being overlooked here.

This sum is not exact, since the $\mathbf{k}$ sum extends only over the Brillouin zone. This gives

$$V_{cc}(\mathbf{l}_{12})\xrightarrow[l_{12}\to\infty]{}\frac{q_1q_2}{l_{12}}\left[1-\frac{4\pi\alpha}{1+8\pi\alpha/3}\right]=q_1q_2/l_{12}\epsilon \quad (15)$$

where, for cubic crystals, the dielectric constant is

$$\epsilon=1+\frac{4\pi\alpha}{1-4\pi\alpha/3}. \quad (16)$$

III. CHARGE-DIPOLE

The same type of analysis is applied to the interaction of an impurity charge q at $\mathbf{l}_1$ and an impurity dipole $\boldsymbol{\mu}$ at $\mathbf{l}_2$, both assumed to be at interstitial sites. The Hamiltonian is

$$\mathcal{H}=+q\frac{\mathbf{l}_{21}\cdot\boldsymbol{\mu}}{l_{12}{}^3}-q\sum_j\frac{\mathbf{l}_{1j}\cdot\mathbf{P}_j}{l_{1j}{}^3}+\sum_j\boldsymbol{\mu}\cdot\varphi_{2j}\cdot\mathbf{P}_j +\tfrac{1}{2}\sum_{ij}\mathbf{P}_i\cdot\boldsymbol{\phi}_{ij}\cdot\mathbf{P}_j.$$

Again eliminating the $\mathbf{P}_j$ coordinates, the effective interaction is

$$V_{cd}=+q\left[\frac{\mathbf{l}_{21}}{l_{12}{}^3}-V_0\sum_j\frac{\mathbf{l}_{j1}\cdot\boldsymbol{\alpha}_j\cdot\boldsymbol{\phi}_{j2}}{l_{1j}{}^3} +V_0{}^2\sum_{ij}\frac{\mathbf{l}_{j1}\cdot\boldsymbol{\alpha}_j\cdot\boldsymbol{\phi}_{ji}\cdot\boldsymbol{\alpha}_i\cdot\boldsymbol{\phi}_{i2}}{l_{1j}{}^3}-\cdots\right]\cdot\boldsymbol{\mu}. \quad (17)$$

In order to convert this to a dipole sum, another wave-vector transform must be defined:

$$\mathbf{T}'(\mathbf{k})=\frac{V_0}{4\pi}\sum_{\mathbf{l}}e^{i\mathbf{k}\cdot(\mathbf{l}-\mathbf{l}_0)}\boldsymbol{\phi}(\mathbf{l}-\mathbf{l}_0).$$

Now the sum of terms in (17) for the charge-dipole interaction can also be summed:

$$V_{cd}=+q\left[\mathbf{l}_{21}/l_{12}{}^3-\frac{4\pi}{V}\sum_{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{l}_{21}}\mathbf{W}(\mathbf{k}) \cdot\mathbf{G}(\mathbf{k})\cdot\boldsymbol{\alpha}\cdot\mathbf{T}'(\mathbf{k})\right]\cdot\boldsymbol{\mu}. \quad (18)$$

In the limit of large $\mathbf{l}_{12}$, we replace $\mathbf{G}(\mathbf{k})$ and $\mathbf{T}'$ by their value at $k=0$, and again only the T_3 component enters in (18). When the interstitial moment is at a position of cubic symmetry, the $\mathbf{k}\to 0$ limit of $T_3'(\mathbf{k})$ is also $\frac{2}{3}$, which gives

$$V\underset{cd}{\to}+q\mathbf{l}_{21}\cdot\boldsymbol{\mu}/l_{12}{}^3(1+8\pi\alpha/3).$$

Using the definition of ϵ,

$$V\underset{cd}{\to}+q\left(\frac{\epsilon+2}{3\epsilon}\right)\mathbf{l}_{21}\cdot\boldsymbol{\mu}/l_{12}{}^3. \quad (19)$$

The long-range interaction is altered by $(\epsilon+2)/3\epsilon$.

IV. DIPOLE-DIPOLE

The effective interaction between two impurity dipoles $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ at $\mathbf{l}_1$ and $\mathbf{l}_2$ is now derived by the same methods. The Hamiltonian and resulting effective interaction are

$$\mathcal{H}=\boldsymbol{\mu}_1\cdot\boldsymbol{\phi}_{12}\cdot\boldsymbol{\mu}_2+\sum_j\boldsymbol{\mu}_1\cdot\boldsymbol{\phi}_{1j}\cdot\mathbf{P}_j+\sum_j\boldsymbol{\mu}_2\cdot\boldsymbol{\phi}_{2j}\cdot\mathbf{P}_j +\tfrac{1}{2}\sum_{ij}\mathbf{P}_i\cdot\boldsymbol{\phi}_{ij}\cdot\mathbf{P}_j,$$

$$V_{dd}=\boldsymbol{\mu}_1\cdot[\boldsymbol{\phi}_{12}-V_0\sum_j\boldsymbol{\phi}_{1j}\cdot\boldsymbol{\alpha}_j\cdot\boldsymbol{\alpha}_{j2} +V_0{}^2\sum_{ij}\boldsymbol{\phi}_{1j}\cdot\boldsymbol{\alpha}_j\cdot\boldsymbol{\phi}_{ji}\cdot\boldsymbol{\alpha}_i\cdot\boldsymbol{\phi}_{i2}+\cdots]\cdot\boldsymbol{\mu}_2, \quad (20)$$

$$V_{dd}=\boldsymbol{\mu}_1\cdot\left[\boldsymbol{\phi}_{12}-\frac{4\pi}{V}\sum_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{l}_{21}}4\pi\mathbf{T}'(\mathbf{k}) \cdot\mathbf{G}(\mathbf{k})\cdot\boldsymbol{\alpha}\cdot\mathbf{T}'(\mathbf{k})\right]\cdot\boldsymbol{\mu}_2. \quad (21)$$

For cubic crystals, the wave-vector sum simplifies to

$$V_{dd}=\boldsymbol{\mu}_1\cdot\left[\boldsymbol{\phi}_{12}-4\pi\alpha\frac{4\pi}{V}\sum_k e^{i\mathbf{k}\cdot\mathbf{l}_{12}}\sum_{\alpha=1}^{3}\frac{\hat{e}_\alpha\hat{e}_\alpha T_\alpha'(\mathbf{k})^2}{1+4\pi\alpha T_\alpha(\mathbf{k})}\right]\cdot\boldsymbol{\mu}_2. \quad (22)$$

In the limit of large $\mathbf{l}_{12}$, V_{dd} is obtained from the approximation

$$\frac{4\pi}{V}\sum_k e^{i\mathbf{k}\cdot\mathbf{l}}\hat{k}\hat{k}=\boldsymbol{\phi}(\mathbf{l}), \quad (23)$$

which gives

$$V_{dd}\xrightarrow[l_{12}\to\infty]{}\frac{\boldsymbol{\mu}_1\cdot\boldsymbol{\phi}_{12}\cdot\boldsymbol{\mu}_2}{(1+8\pi\alpha/3)(1-4\pi\alpha/3)} =\left(\frac{\epsilon+2}{3}\right)^2\frac{\boldsymbol{\mu}_1\cdot\boldsymbol{\phi}_{12}\cdot\boldsymbol{\mu}_2}{\epsilon}. \quad (24)$$

V. EXTERNAL DIPOLE MOMENT

The exact formulas for the interaction energy, as a function separation $\mathbf{l}_{12}$, have been derived for charge-charge (11), charge-dipole (18), and dipole-dipole (21) Coulomb interactions in molecular solids. For small values of $\mathbf{l}_{12}$, the indicated wave-vector sum would have to be done numerically to obtain the proper separation dependence. The asymptotic form of the interactions, valid for large $\mathbf{l}_{12}$, are given in (15), (19), and (24).

After noting the occurrence of the $(\epsilon+2)/3$ factor in the interactions involving dipoles, it seems reasonable to define the external dipole moment as

$$\boldsymbol{\mu}_e=\tfrac{1}{3}(\epsilon+2)\boldsymbol{\mu}.$$

This causes the effective interaction to have the forms given in Table I. All interactions are now just reduced by ϵ^{-1}, as one expects Coulomb interactions to be reduced. The other $(\epsilon+2)/3$ factors show that the ions near the impurity dipole polarize around it to make its external moment look larger. Thus, for any type of equation, wherever $\boldsymbol{\mu}$ appears in the formulas for interaction in a vacuum, then $\boldsymbol{\mu}_e$ should be used for interactions in a cubic dielectric. An additional check is to evaluate the interaction of a dipole μ, between the parallel plates of a condenser, with the internal field $E_{\text{int}}=V/d$; the result $-\boldsymbol{\mu}\cdot\mathbf{E}_{\text{int}}$ for a vacuum does become $-\boldsymbol{\mu}_e\cdot\mathbf{E}_{\text{int}}$ in the dielectric.[11] This form of the external field is different than that deduced from the classical models of Onsager[1] and Fröhlich.[3] This suggests, perhaps, that their classical models are also incorrect for liquids.

VI. SUBSTITUTIONAL IMPURITIES

In the preceding discussion of local-field corrections, the charges were conveniently assumed to be interstitial impurities. This meant that the dielectric response of the host lattice was undisturbed by the presence of the impurities. When an impurity occupies a lattice site, a host ion is missing. Its absence alters the local dielectric response of the system.

These changes occur in the higher order terms in the effective interactions. For example, the third term in the series (6) for the charge-charge interaction is now written

$$V_0^2\sum_{\substack{i,j\\ i\neq 1\\ j\neq 2}}\frac{\mathbf{l}_{1j}\cdot\boldsymbol{\alpha}_j\cdot\boldsymbol{\phi}_{ji}\cdot\boldsymbol{\alpha}_i\cdot\mathbf{l}_{i2}}{l_{1j}^3l_{i2}^3}=V_0^2\sum_{i,j}\frac{\mathbf{l}_{1j}\cdot\boldsymbol{\alpha}_j\cdot\boldsymbol{\phi}_{ji}\cdot\boldsymbol{\alpha}_i\cdot\mathbf{l}_{12}}{l_{1j}^3l_{i2}^3}$$
$$-2V_0^2\sum_i\frac{\mathbf{l}_{12}\cdot\boldsymbol{\alpha}_2\cdot\boldsymbol{\phi}_{2i}\cdot\boldsymbol{\alpha}_i\cdot\mathbf{l}_{i2}}{l_{12}^3l_{i2}^3}+V_0^2\frac{\mathbf{l}_{12}\cdot\boldsymbol{\alpha}_2\cdot\boldsymbol{\phi}_{21}\cdot\boldsymbol{\alpha}_1\cdot\mathbf{l}_{12}}{l_{12}^6}. \tag{25}$$

The effect of the first correction term in (25) is to assign the charge q_2 an effective dipole moment

$$\mathbf{d}_2=2q_2V_0^2\sum_i\boldsymbol{\phi}_{2i}\cdot\boldsymbol{\alpha}_i\cdot\mathbf{l}_{i2}/l_{i2}^3. \tag{26}$$

This moment is zero in cubic crystals because of the cancellation of $\mathbf{l}$ and $-\mathbf{l}$ terms. The higher order terms in the series (6) each have a rapidly increasing number of such correction terms. All of these correction terms to the charge-charge interaction correspond to corrections to the l^{-1} term of the order l^{-2} or higher. They can be safely omitted in the limit $l\rightarrow\infty$.

These corrections are important for the charge-dipole and dipole-dipole interactions. An examination of these terms shows that some of them go with the same power of $\mathbf{l}$ as the fundamental interactions. Other correction terms go with l^{-3n} higher powers of $\mathbf{l}$. The important terms with the same $\mathbf{l}$ dependence can be conveniently expressed as an alteration of the effective dipole moment. Their effect is to replace the moment $\boldsymbol{\mu}$ by[22]

$$\boldsymbol{\mu}'=\boldsymbol{\mu}\cdot[\mathbf{I}-V_0^2\alpha^2\sum_i\boldsymbol{\phi}_{1j}\cdot\boldsymbol{\phi}_{j1}$$
$$+V_0^3\alpha^3\sum_{ij}\boldsymbol{\phi}_{1j}\cdot\boldsymbol{\phi}_{ji}\cdot\boldsymbol{\phi}_{i1}-\cdots], \tag{27}$$

which may be written as a wave-vector sum

$$\boldsymbol{\mu}'=\boldsymbol{\mu}\cdot\left[\mathbf{I}-\frac{(4\pi\alpha)^2}{N}\sum_k\mathbf{T}(\mathbf{k})\cdot\mathbf{G}(\mathbf{k})\cdot\mathbf{T}(\mathbf{k})\right].$$

Since $\boldsymbol{\mu}'$ enters into all formulas, it is just the measured moment. These correction terms can be evaluated by numerical integration. Their magnitude can be estimated from the first term, which is also the leading lattice sum in calculations on van der Waals binding energies.[17] For dipole interactions at large distance, the total external moment is now

$$\boldsymbol{\mu}_e'=\tfrac{1}{3}(\epsilon+2)\boldsymbol{\mu}'.$$

It is obvious from (27) that the ratio $\boldsymbol{\mu}'/\mu$ depends upon the dielectric constant ϵ. Numerical integration of the wave-vector sum in (27) is necessary in order to determine this ϵ dependence.

No simple approximation scheme seems possible, since the functions $T_j(k)$ vary considerably near the edge of the Brillouin zone, where the density of wave-vector states is large. It is discouraging to note that Doniach's[13] ingenious method of approximating a similar integral has been shown to lead to large errors by Lucas's[16] numerical calculations.

Another change which occurs for substitutional impurities is that $\mathbf{W}(\mathbf{k})$ is now defined as

$$\mathbf{W}(\mathbf{k})=\frac{V_0}{4\pi}\sum_{\mathbf{l}\neq 0}e^{i\mathbf{k}\cdot\mathbf{l}}\mathbf{l}/l^3.$$

One should also use $\mathbf{T}(\mathbf{k})$ instead of $\mathbf{T}'(\mathbf{k})$.

In this case, (18) and (21), simplify to

$$V_{\text{cd}}=+q\frac{(4\pi)}{V}\sum_k e^{-i\mathbf{k}\cdot\mathbf{l}_{21}}\mathbf{W}(\mathbf{k})\cdot\mathbf{G}(\mathbf{k})\cdot\boldsymbol{\mu}', \tag{18'}$$

$$V_{\text{dd}}=\frac{4\pi}{V}\sum_k e^{i\mathbf{k}\cdot\mathbf{l}_{21}}\boldsymbol{\mu}_1'\cdot\mathbf{T}(\mathbf{k})\cdot\mathbf{G}(\mathbf{k})\cdot\boldsymbol{\mu}'_2. \tag{21'}$$

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[22] If the polarizability of the impurity α' is nonzero, then $\alpha^2\rightarrow\alpha(\alpha-\alpha')$, $\alpha^3\rightarrow\alpha^2(\alpha-\alpha')$, etc. Thus, in (27), the factor $(4\pi\alpha)^2\rightarrow(4\pi)^2\alpha(\alpha-\alpha')$.

These formulas have the same $l \to \infty$ as the prior results shown in Table I. The only change is the use of $\boldsymbol{\mu}'$ instead of $\boldsymbol{\mu}$.

VII. DISCUSSION

An attempt was made to estimate the distance at which the limiting forms (15), (19), and (24) become valid. This effort was abandoned when it was realized that the most important correction terms arose from the approximations (14) and (23). By replacing the wave-vector sum over the Brillouin zone by a sum to infinity, one introduces errors which depend upon the shape of the zone.

The effective mass of exciton states in cubic crystals was also evaluated. These masses arise from the wave-vector dependence of

$$T(\mathrm{k})_{\alpha\beta}=\frac{k_\alpha k_\beta}{k^2}-\tfrac{1}{3}\delta_{\alpha\beta}+k_\lambda k_\delta w_{\alpha\beta\lambda\delta}(a/\pi)^2+0(k^4).$$

The lattice constant a is introduced to make w dimensionless, and therefore dependent only upon crystal structure. The value used for a was the molecular separation along a $\langle 100\rangle$ direction. The fourth-order inverse effective-mass tensor w has the general form for cubic crystals. It contains three independent constants w_{11}, w_{12}, and w_{44}. The condition that Trace $\mathbf{T}(\mathbf{k})=0$ imposes the condition $w_{11}+2w_{12}=0$. The exciton mass is characterized by two constants, w_{11} and w_{44}. These are $w_{11}=-0.291$ and $w_{44}=-0.093$ in bcc lattices, $w_{11}=-0.187$ and $w_{44}=-0.057$ in fcc lattices, and $w_{11}=0.258$ and $w_{44}=-0.501$ in sc lattices. These values are in agreement with calculations of $\mathbf{T}(\mathbf{k})$ over the entire Brillouin zone.[16]

This method of evaluating local-field corrections can also be applied to solids composed of several different kinds of atoms. Here the single equation (10b) for $\mathbf{G}$ is replaced by a set of coupled equations—the number of equations equals the number of different atoms. A calculation on NaCl structures gives the obvious result that the polarizability α to use in ϵ is just the sum of the anion and cation polarizabilities.

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