# Dielectric Screening of Coulomb Interactions in Polymers

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ABSTRACT: A formula is presented for the treatment of the effective electrostatic interaction energy between charges in a polymeric material. The result of a many-electron perturbation-theoretic analysis suggests that a reasonable approximation to the effective interaction is given by reducing the bare interaction by a factor equal to the reciprocal of the macroscopic dielectric constant. A more precise result is given in terms of a spatially varying screening function.

## 1. Introduction

Attempts to predict the equilibrium conformation of macromolecules begin with a calculation of the energies of possible structures. Of the various terms that may contribute to the energy, the Coulomb interaction between atoms carrying electric charges is at the same time one of the largest and one of the terms about whose calculation there is least confidence. This uncertainty is reflected in the literature, where one finds a wide variety of approaches.[3-18] The essence of the difficulty lies in the question of the role of all the other atoms in the structure. Do they act as components of a dielectric medium and hence reduce the effective force between charges by some numerical constant, or is it inappropriate to apply such macroscopic concepts on an atomic scale?

One of the earliest approaches to this problem of relating macroscopic and microscopic models of the response of matter to an electric field is that of Clausius[3] and Mossotti,[4] in which the macroscopic polarization of the medium is the sum of the polarizations of the individual components of the medium due to the actual local fields to which those individual components are subjected. The local field is usually taken to be the macroscopic field due to the dielectric medium outside a sphere which divides the local and distant portions of the medium, with the assumption that the contribution from the local region vanishes. Application of this approach requires knowledge of the microscopic polarizability, however.

Many authors currently performing conformational calculations treat the dielectric function as a constant. Hammarström et al.[10] take the dielectric constant to be unity, while other authors have used the bulk value of the dielectric constant.[5,9,12] Tonelli[6,13] adjusts the value of the dielectric constant to best fit his conformational energy calculation to experimental data. Hanes,[7] recognizing that at extremely short distances between charges there should be no dielectric modification of the Coulomb interaction since little of the medium can be situated between the charges, assumes that the dielectric function is proportional to $r$, the distance between the charges, for all values of $r$. Hopfinger[8] assumed a model for the spatial dependence of the dielectric function in which the dielectric function starts at unity when the charges are close and grows linearly with the distance between the charges until it reaches the bulk dielectric constant. Finally, some authors[16-18] choose to model dielectric effects by imagining permanent dipoles and induced dipoles placed at bond sites and evaluating the magnitudes, directions, and exact locations of the dipoles by fitting the model to experimental data, a new fit being required for each new molecular situation. While such an approach is naturally more powerful than any simple choice of a dielectric function can be, its implementation is arduous, and there remains a need for a simpler and more practical approximation scheme for general use. It is within this context that the confusion (or, indeed, exasperation) over the choice of dielectric constant was concisely voiced by Clark et al.,[11] who chose to omit entirely the electrostatic potential from their work, citing "ambiguity in calculation of the charges, the dielectric functions, and the attenuation functions, or cutoffs".

In this paper we attempt an answer to the problem of calculating the energy of interaction of a pair of fixed charges embedded in a molecular solid. We do not address the question of the origin of these charges and do not allow the position of the nucleus of any atom to change in response to the fields due to these charges. We thus consider only the response of all the electrons in the system to the presence of the two introduced charges. Because our goal is the evaluation of an effective dielectric constant to modify the Coulomb interaction of the charges, we also consider only terms that are linear in the magnitude of these charges.

The first question to answer is whether there is any need at all for a correction of this kind to the Coulomb energy of interaction. If we were to consider the force between a sodium ion and a distant chlorine ion in a crystal of NaCl, for example, we could argue that there should be little or no screening by any intervening ions. The symmetry of the crystal structure of NaCl ensures that each ion experiences no net electric field and is consequently not polarized. Since the presence of a dielectric constant represents the reduction in electrostatic energy due to polarization of the medium, there is clearly no need for a correction to the Coulomb energy of the bare ions.

This argument, however, is fallacious when applied to systems lacking the symmetry of NaCl. To see this, one need only consider the case of two ions embedded in a metal. It is quite clear that the energy of the system is unaffected by motion of one of the ions as long as it is separated from the other ion by more than a few lattice spacings.

There is thus clearly a need for some type of correction to the Coulomb energy of interaction of charges within a medium. At large distances a reduction in this energy must occur, while at the smallest of distances no significant amount of electron charge can interpose itself between the two embedded ions, and no reduction exists. The appropriate formalism is thus one which has the concept of a range-dependent dielectric constant at its core. If the ions are located at $\vec{R}_1$ and $\vec{R}_2$, then a dielectric constant of the form $\epsilon(\vec{R}_1,\vec{R}_2)$ will provide all the information needed for an accurate description of the effective Coulomb energy of interaction.

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While the concept of a dielectric constant dependent on $\vec{R}_1$ and $\vec{R}_2$ is valuable in providing an understanding of the form of the response of a macromolecular system of embedded point charges, it is not very helpful in facilitating practical calculations, and some approximation is necessary. The most useful simplification that we can make is to assume that $\epsilon(\vec{R}_1,\vec{R}_2)$ can be approximated by a function of only the separation of the ions, $\vec{R} = \vec{R}_1 - \vec{R}_2$. This assumption of translational invariance in the problem is tantamount to an averaging of the electron density over space and allows us to work in the familiar formalism of a wavenumber-dependent dielectric constant $\epsilon(q)$.

In the analysis that follows we will make a further approximation for the sake of simplicity in the exposition. We shall assume isotropy of the system and consider $\epsilon$ a function only of $R$, the magnitude of $\vec{R}$. In the case of highly anisotropic systems, such as conjugated polymers, this will be inappropriate. A tensor form of $\epsilon$ must then be used in a simple generalization of the theory presented below.

## 2. Formalism

We take as our starting point the Hamiltonian for a system consisting of two ions, of charges $Q_1$ and $Q_2$, placed a distance $R$ apart in a macromolecular medium in which interacting electrons move in a spatially varying potential. We write

$$\mathcal{H} = \mathcal{H}_{\text{ion-ion}} + \mathcal{H}_1$$

where

$$\mathcal{H}_{\text{ion-ion}} = \frac{Q_1 Q_2}{4\pi\epsilon_0 R} \tag{2.1}$$

$$\mathcal{H}_1 = \mathcal{H}_0 + \mathcal{H}_{\text{ion-electron}} + \mathcal{H}_{\text{electron-electron}} \tag{2.2}$$

with $\mathcal{H}_0$ the Hamiltonian for independent electrons moving in the potential of the macromolecules and $\epsilon_0$ the permittivity of the vacuum. In the language of second quantization[19] we can write

$$\mathcal{H}_{\text{ion-electron}} = \sum_{k,q} [U_1(q) + U_2(q)] c^{\dagger}_{k+q} c_k \tag{2.3}$$

with $U_1(q)$ the Fourier transform of the potential due to the ion of charge $Q_1$ and with $c^{\dagger}$ and $c$ the creation and annihilation operators for electrons. Finally

$$\mathcal{H}_{\text{electron-electron}} = \frac{1}{2} \sum_{k,k',q} V_q c^{\dagger}_{k-q} c^{\dagger}_{k'+q} c_{k'} c_k \tag{2.4}$$

with $V_q$ the Fourier transform of the Coulomb potential. For a system of volume $\Omega$ we have $V_q$ equal to $e^2/(\Omega\epsilon_0 q^2)$.

Our goal is to calculate the variation of the energy $\mathcal{E}$ of the system described by $\mathcal{H}_1$ in terms of $Q_1$, $Q_2$, and $R$. We start by noting that, in the limit of large $R$, the energy will consist of terms containing various powers of $Q_1$, $Q_2$, and $V_q$ but no cross terms containing both $Q_1$ and $Q_2$. As we bring the charges together, the energy will be changed by the screened interaction of the charges. In the lowest significant order of perturbation theory we will then find a term of the form $Q_1Q_2f(R)$. The approach to the problem in terms of a position-dependent or wavenumber-dependent dielectric constant thus requires only a calculation of this particular term in the perturbation-theoretic expansion of the energy $\mathcal{E}$.

The only nonvanishing terms in the expansion of this part of $\mathcal{E}$ will be of the form

$$\langle \Phi | V G_0 V G_0 \ldots V G_0 \mathcal{H}_{\text{ion-electron}} G_0 V \ldots V G_0 \mathcal{H}_{\text{ion-electron}} G_0 V \ldots G_0 V | \Phi \rangle \tag{2.5}$$

where $V$ is our abbreviation for $\mathcal{H}_{\text{electron-electron}}$ and $G_0 = (\mathcal{E} - \mathcal{H}_1)^{-1}$. The action of all possible powers of $G_0V$ acting on the unperturbed wave function $|\Phi\rangle$ then gives us the wave function $|\Psi\rangle$ of the interacting system in the absence of the embedded ions. Summing over all powers of $G_0V$ then gives an expression for the energy perturbation of the form

$$Q_1Q_2f(R) = \sum_{k,q} \langle \Psi | U_1(q)\, c^{\dagger}_{k+q} c_k G_0 (1 - VG_0)^{-1} \times U_2(-q)\, c^{\dagger}_k c_{k+q} | \Psi \rangle \tag{2.6}$$

We make the random-phase approximation[20] of allowing momentum exchange between electrons only in amounts of $\hbar q$ and find

$$Q_1Q_2f(R) = \sum_q U_1(q)\, U_2(-q) \left\langle \Psi \middle| \left( \sum_k \frac{n_{k+q} - n_k}{\mathcal{E}_{k+q} - \mathcal{E}_k} \right) \times \left( 1 - V_q \sum_k \frac{n_{k+q} - n_k}{\mathcal{E}_{k+q} - \mathcal{E}_k} \right)^{-1} \middle| \Psi \right\rangle \tag{2.7}$$

With the definition

$$\epsilon(q) \equiv 1 - \frac{e^2}{\Omega\epsilon_0 q^2} \sum_k \frac{\langle \Psi | n_{k+q} - n_k | \Psi \rangle}{\mathcal{E}_{k+q} - \mathcal{E}_k} \tag{2.8}$$

we find

$$Q_1Q_2f(R) = \sum_q U_1(q)\, U_2(-q) \frac{\Omega\epsilon_0 q^2}{e^2} \left( \frac{1}{\epsilon(q)} - 1 \right) \tag{2.9}$$

Since

$$U_1(q) = \frac{eQ_1}{\Omega\epsilon_0 q^2} e^{i\vec{q}\cdot\vec{R}_1}$$

and

$$U_2(q) = \frac{eQ_2}{\Omega\epsilon_0 q^2} e^{i\vec{q}\cdot\vec{R}_2}$$

we have

$$Q_1Q_2f(R) = \sum_q \frac{Q_1Q_2}{\Omega\epsilon_0 q^2} \left( \frac{1}{\epsilon(q)} - 1 \right) e^{i\vec{q}\cdot(\vec{R}_1 - \vec{R}_2)} \tag{2.10}$$

To this must be added the contribution of $\mathcal{H}_{\text{ion-ion}}$, which cancels the second term in the parentheses. We are then left with the net energy perturbation $\mathcal{E}_{12}$ due to the embedded charges as given by

$$\mathcal{E}_{12} = \frac{Q_1Q_2}{\Omega\epsilon_0} \sum_q \frac{e^{i\vec{q}\cdot\vec{R}}}{q^2\epsilon(q)} \tag{2.11}$$

The problem of the effective interaction is thus reduced to that of calculating $\epsilon(q)$ as defined in eq 2.8. If $\epsilon$ were independent of wavenumber, then the interaction energy would reduce to the simple form $Q_1Q_2/(4\pi\epsilon_0\epsilon R)$ assumed by some workers.

## 3. Calculating $\epsilon(q)$

While the derivation of the form of $\epsilon(q)$ has received a great deal of attention in the context of metallic systems,[21] there have been relatively few calculations for organic materials. For simple crystalline semiconductors one may make use of the periodicity of the lattice to develop methods based on band-structure calculations or the method of density functionals.[22-25] In glassy and liquid materials, the periodicity of the lattice is lost, and the few treatments to be found in the literature involve statistical arguments relating to the disordered nature of these materials.[26-29]

Because our goal is the derivation of an approximate form for $\epsilon(q)$ that will be useful in calculation of the conformational energy of macromolecules, we seek a description of $\epsilon(q)$ in terms of a very small number of parameters. If estimating the values of these parameters were to require extensive calculation, then we would be defeating the object of developing an accessible technique for calculating Coulomb energies. We thus seek a simple model for $\epsilon(q)$ capable of being expressed in terms of two or three available characteristics of the macromolecular system.

The two key quantities governing the electronic structure of an insulator are the gap in energy, $V_g$, between valence and conduction bands, and the density $n$ of electrons in the valence band, which is related to the plasma frequency $\omega_p$ through the relationalship

$$\omega_p{}^2 = ne^2/\epsilon_0 m \qquad (3.1)$$

with $m$ the electron mass. We accordingly look for a reasonable approximation for $\epsilon(q)$ that will depend on only these two quantities.

For Bloch electrons in a lattice, expression (2.8) is modified from its free-electron form.[30] The presence of an electronic band structure now has as a consequence the existence of both intraband and interband contributions to $\epsilon(q)$. In an insulator the intraband terms vanish, since the occupancy $n_k$ of valence-band states is unity, and $n_{k+q} - n_k$ is always zero. In the case of a metallic conductor, it was precisely these terms that dominated for small $q$, since the intraband sum tends to a constant while the Coulomb factor of $q^{-2}$ causes a divergence. In an insulator, on the other hand, the only surviving terms are the interband contributions, of which we retain only those linking states in the valence band, of energy $\mathcal{E}_{k+q,v}$, with states in the conduction band of energy $\mathcal{E}_{k,c}$. We then have

$$\epsilon(q) = 1 - \frac{e^2}{\Omega\epsilon_0 q^2}\sum_k \frac{|M_{cv}(q)|^2}{\mathcal{E}_{k+q,v} - \mathcal{E}_{k,c}} \qquad (3.2)$$

where

$$M_{cv}(q) \equiv \int \psi^*_{k+q,v} e^{-i\vec{q}\cdot\vec{r}} \psi_{k,c}\, \mathrm{d}\vec{r} \qquad (3.3)$$

and is the matrix element for interband scattering by a periodic potential of wavenumber $\vec{q}$. In the limit of small $q$

$$M_{cv}(q) = \vec{q}\cdot\int \psi^*_{k,v} \frac{\partial\psi_{k,c}}{\partial\vec{k}}\, \mathrm{d}\vec{r}$$
$$\sim q/k_1 \qquad (3.4)$$

where

$$k_1 = (mV_g{}^2/\hbar^2\mathcal{E}_F)^{1/2} \qquad (3.5)$$

with $\mathcal{E}_F$ the average kinetic energy of the valence-band electrons. The qualitative form of $\epsilon(q\rightarrow 0)$ is found by treating the summand in eq 3.2 as a constant equal to $q^2/(k_1{}^2V_g)$ over a fraction $V_g/\mathcal{E}_F$ of the Brillouin zone and zero elsewhere. Making use of the fact that $n = N/\Omega$, with $N$ the number of states included in the sum, we then find the familiar result[31,32]

$$\epsilon(q\rightarrow 0) \approx 1 + (\hbar\omega_p/V_g)^2 \qquad (3.6)$$

For large $q$ the expression for $\epsilon(q)$ approaches asymptotically the free-electron Lindhard form,[33] so that

$$\epsilon(q\rightarrow\infty) \approx 1 + (\hbar\omega_p/\mathcal{E}_q)^2 \qquad (3.7)$$

with $\mathcal{E}_q = \hbar^2q^2/(2m)$. Comparison of expressions (3.6) and (3.7) suggests that an appropriate approximation to $\epsilon(q)$ over its entire range would be the interpolation formula

$$\epsilon(q) = 1 + \left(\frac{\hbar\omega_p}{V_g + \mathcal{E}_q}\right)^2 \qquad (3.8)$$

## 4. Screening Function $\epsilon(R)$

With the aid of expression (3.8) we are now in a position to propose a form for the effective dielectric constant to be used in calculations of Coulomb interactions in macromolecular assemblies. We define a screening function $\epsilon(R)$ for the interaction of two charges $Q_1$ and $Q_2$ through the expression

$$\mathcal{E}_{12} = \frac{Q_1Q_2}{4\pi\epsilon_0 R\epsilon(R)} \qquad (4.1)$$

being careful to note that $\epsilon(R)$ is *not* simply the Fourier transform of $\epsilon(q)$ but is evaluated by identifying eq 4.1 with eq 2.11. Comparison of these two expressions then gives us the result

$$\frac{1}{\epsilon(R)} = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\sin(qR)}{qR\epsilon(q)}\, \mathrm{d}(qR) \qquad (4.2)$$

We simplify the integrand by defining the macroscopic dielectric constant as

$$\epsilon(q\rightarrow 0) \equiv \epsilon_m$$

and

$$2mV_g/\hbar^2 \equiv \kappa^2$$

so that, from eq 3.8

$$\frac{1}{\epsilon(q)} = 1 - \frac{(\epsilon_m - 1)\kappa^4}{\kappa^4(\epsilon_m - 1) + (\kappa^2 + q^2)^2} \qquad (4.3)$$

The integral in eq 4.2 is then evaluated[34] to yield the result

$$\frac{1}{\epsilon(R)} = \frac{1}{\epsilon_m} + \left(1 - \frac{1}{\epsilon_m}\right)e^{-\tilde{\kappa}R\cos t}\,\frac{\sin(\tilde{\kappa}R\sin(t) + 2t)}{\sin(2t)} \qquad (4.4)$$

where

$$t = \frac{1}{2}\arccos(\epsilon_m{}^{-1/2}); \quad \tilde{\kappa} = \kappa\epsilon_m{}^{1/4} \qquad (4.5)$$

This result is plotted in Figure 1, where $1/\epsilon(R)$ is given as a function of $\kappa R$ for the cases where $\epsilon_m = 2.2$ and $\epsilon_m = 4$. One sees from these illustrations that the oscillatory part of expression (4.4) is unimportant, as the exponential factor has reduced the contribution of these terms to a negligible amplitude before their oscillatory nature becomes apparent.

## 5. Implementation

We now have in eq 4.4 a simple and general formula with which to approximate the effects of dielectric screening of the Coulomb interaction in insulating organic materials. The principal remaining issue is whether the application of this result can be made sufficiently straightforward to be of widespread usefulness.

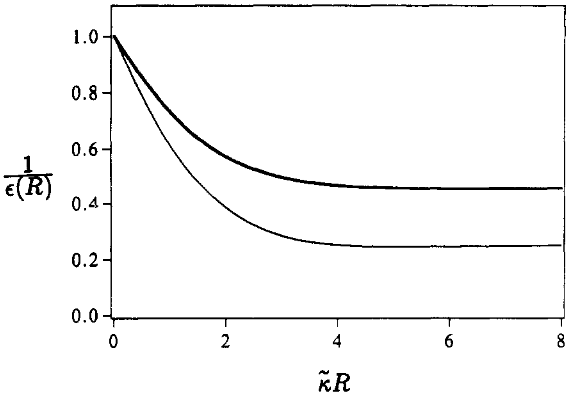

**Figure 1.** Graphs showing the factor by which the Coulomb interaction between charges is reduced by dielectric screening as a function of the scaled distance $\tilde{\kappa}R$ between charges. In the two cases shown the macroscopic dielectric constant $\epsilon_m$ is equal to 2.2 (bold line) and 4 (thin line), respectively.

As expressed in eq 4.4, the screening function depends on the two parameters $\epsilon_m$ and $\tilde{\kappa}$. These in turn were expressed in terms of the plasma frequency $\omega_p$ and the average energy gap $V_g$ between valence and conduction bands. The plasma frequency was defined in terms of the density of valence electrons and thus is the simplest of these parameters to compute. One then needs only one other parameter, and a choice may be made between estimating $V_g$ or $\epsilon_m$. For nonconjugated polymers $V_g$ is typically[35] at least 6 eV, or 600 kJ mol$^{-1}$. For such a value of $V_g$ we would then find $\tilde{\kappa}$, which determines the length scale of the screening, to be about $13\epsilon_m^{1/4}$ nm$^{-1}$. The fractional power to which $\epsilon_m$ is raised in this expression makes $\tilde{\kappa}$ insensitive to the precise value of $\epsilon_m$, and so for many materials we would find $\tilde{\kappa}$ to be no less than about 16 nm$^{-1}$.

The significance of the form of $\epsilon(R)$ shown in Figure 1 becomes apparent when we realize that steric hindrance seldom allows unbonded atoms to approach each other closer than about 0.2 nm. The minimum value of $\tilde{\kappa}R$ at which one needs to calculate the Coulomb interaction is thus about 3.2. From Figure 1 we see that when $\tilde{\kappa}R \geq 3.2$, the screening has come close to reaching its asymptotic value for large distances. It is thus not necessary to know the value of $\kappa$ with any great precision in order to estimate the effective Coulomb interaction; the crucial quantity is the macroscopic dielectric constant $\epsilon_m$.

If one has no experimental information concerning the dielectric properties of a material for which an energy calculation is to be performed, one may make use of the fact that for most organic materials the refractive index is not very different from 1.5. Since the high-frequency dielectric constant is approximately equal to the square of the refractive index, a value for $\epsilon_m$ of 2.2 will be a possible choice in the absence of other information. However, because of the many approximations made in this theory one will not necessarily find consistency between this value and one found from eq 3.6.

## 6. Conclusions

We have seen that many-electron theory can be used to derive an approximate expression for the effective Coulomb interaction between pairs of charges in an insulating organic solid. While the formal expression for the screening function, $\epsilon(R)$, is complicated, we find that a number of simple conclusions may be drawn.

1. It *is* necessary to include dielectric screening in any calculation of the effective interaction between charges in a macromolecular solid.

2. A reasonable approximation to the Coulomb interaction at all normally occurring values of the interatomic separation $R$ is to divide the unscreened interaction energy by the macroscopic dielectric constant $\epsilon_m$.

3. A more accurate expression for the effective interaction is obtained by use of eq 4.4. This, however, requires knowledge of the parameter $\tilde{\kappa}$, which is related to the average direct energy gap between valence and conduction bands.

4. In the absence of specific knowledge of $\epsilon_m$ and $\tilde{\kappa}$, one may use the "generic" values of $\epsilon_m = 2.2$ and $\kappa = 16$ nm$^{-1}$ in eq 4.4 to provide an approximate expression for the screening function.

Finally, we draw attention to the inadequacies of the treatment presented here. Coulomb interactions in systems containing several components of different dielectric properties cannot readily be evaluated with our model. In addition to the assumptions of isotropy and translational invariance, our model neglects all complexities of band structure, electron–phonon interactions, and exchange and correlation. Conjugated polymers will in particular be sufficiently anisotropic as to be outside the range of validity of this treatment. In addition, we have not addressed the question of the origin of the charges between which interactions occur. We recognize that the effective charge on an atom is itself a variable and subject to the effects of local electric fields. The preceding theory is presented merely as a simple first step on the path toward a systematic treatment of the screening of Coulomb interactions in polymers.

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