



# The behaviour of charge distributions in dielectric media



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## ABSTRACT

Screened Coulomb interaction in dielectrics is often used as an argument for a lower exciton binding energy and easier exciton dissociation in a high dielectric material. In this paper, we show that at length scales of excitons (10–20 Å), the screened Coulomb law is invalid and a microscopic (quantum chemical) description is necessary to describe the medium effect on exciton dissociation. The exciton dissociation energy decreases with increasing dielectric constant, albeit deviating from the inversely proportional relationship. The electron–hole interaction energy, approximated with a point charge model, is apparently not affected by the dielectric constant of the environment.

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## 1. Introduction

In the quest for more efficient organic photovoltaic devices (OPVs), the use of materials with a high dielectric constant has been suggested [1]. One reason why organic photovoltaic systems are less efficient than inorganic solar cells like those based on silicon, is the high exciton binding energy. This is commonly attributed to the low dielectric constant of OPVs ( $\epsilon \approx 4$ ) [2,3]. This idea is based on the screened Coulomb law in ponderable materials, which tells us that the interaction energy and force between point charges embedded in such media are given by, respectively (in atomic units),

$$U_{ij} = \frac{Q_i Q_j}{\epsilon R_{ij}} \quad (1)$$

$$\mathbf{F}_{ij} = \frac{Q_i Q_j (\mathbf{R}_j - \mathbf{R}_i)}{\epsilon R_{ij}^3}; \quad \epsilon \geq 1.0$$

with  $Q_i$  and  $Q_j$  the point charges,  $\mathbf{R}_i$  and  $\mathbf{R}_j$  their positions,  $R_{ij}$  the distance between them and  $\epsilon$  the (relative) dielectric constant of the medium. By definition,  $\epsilon \geq 1.0$ , furthermore,  $\epsilon$  is independent of the type (plus or minus) of the charges, which means that like (+/+, or -/-) and unlike (+/-) interactions are equally reduced as compared to the vacuum situation ( $\epsilon = 1.0$ ). A charge  $Q_i$  in a cavity of radius  $a$ , embedded in an infinite continuum with dielectric

constant  $\epsilon$ , gives rise to an induced charge on the cavity's surface (Born formula [4]):

$$Q_i^* = - \left(1 - \frac{1}{\epsilon}\right) Q_i \quad (2)$$

which is independent of  $a$ . When a second charge ( $Q_j$ ) is introduced, at a distance  $R_{ij}$  so large that the total interaction energy, to first order, can be written as [5]

$$U_{ij} = \frac{1}{R_{ij}} \left[ Q_i Q_j + \frac{1}{2} (Q_i^* Q_j + Q_i Q_j^*) \right] \quad (3)$$

*i.e.*, if the polarisation comes only from the inducing charges separately without cross terms, then Eq. (2) can be inserted in Eq. (3) giving Eq. (1).

Hence, Eq. (1) holds only for *macroscopic* situations, *i.e.*, the charges are averages over macroscopic volumes, although small with respect to the actual size of the system, and therefore should be at *macroscopic* distances (at least about 100 Å [6]) from each other. However, an exciton generated in OPV materials consists of a pair of unlike charges at a separation of 10–20 Å in a molecular, and therefore highly anisotropic, polarisable environment. As a consequence, Eq. (1) should not be used to describe or explain the charge separation: the charges must already be farther separated before the screened Coulomb law is applicable. Hence, it is not straightforward that the charges involved in an exciton behave like they were in a macroscopic dielectric, and a more indepth consideration of their behaviour is necessary to understand charge separation in OPVs better. Therefore, in this contribution, the effective forces between charges and exciton binding energies are studied in different materials, and the consequences for OPVs are discussed.

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The paper is structured as follows: below a short overview is given of studies that are relevant for the topic at hand. In Section 2 the behaviour of point charges in inorganic C and Si clusters is discussed, because the dielectric constants of these materials are known. Subsequently, in Section 3, the dissociation of point charges is modelled in different organic materials. The materials are selected based on their different properties: one is a reference alkane, one material contains dipoles, and one material contains highly polarisable atoms. These materials can serve as side-chains in organic photovoltaic polymers to enhance the dielectric constant. In Section 4, the influence of a dielectricum on the exciton binding in a typical donor–acceptor complex is investigated. In Section 5, the findings of the previous sections are combined for a typical photovoltaic system [7] to investigate the effect of the dielectric constant on the exciton binding energy. Finally, in Section 6, a summary is given of the most important conclusions: the screened Coulomb law is not applicable for the description of an arbitrary collection of charges and polarisabilities and microscopic studies using QM/MM methods are necessary to investigate the effect of the medium on the exciton dissociation.

As early as 1982, Van Duijnen and Thole [8] noted that a dielectric placed *between* two interacting charges increases the interaction ( $\epsilon_{\text{eff}} < 1.0$ ). Later, Rullmann et al. [9] showed that microscopic collections of (point) charges and polarisabilities show behaviour that cannot be described by the simple expression of Eq. (1), while De Vries and Van Duijnen [10] discussed the problems associated with mixing macroscopic and microscopic descriptions of such systems. In microscopic studies where deviations from Eq. (1) were found – charges interacting more than *in vacuo* ( $\epsilon_{\text{eff}} < 1.0$ ), even like charges attracting each other ( $\epsilon_{\text{eff}} < 0.0$ ) – were reported [11–13].

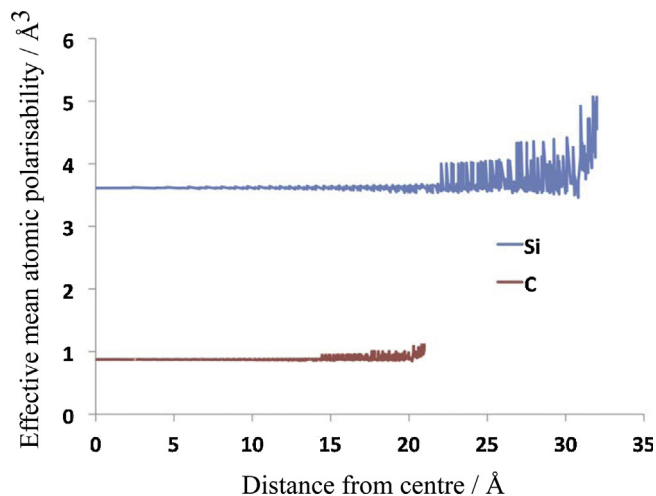
In most efforts for calculating exciton binding energies by applying the Bethe–Salpeter equation the interaction is screened with the (bulk) dielectric constant for interaction distances [14,15] well below the 100 Å mentioned above. Interestingly, Deslippe et al. [16] reported exciton interactions in carbon nanotubes, larger than ‘bare’ interactions, which they coined ‘anti-screening’.

A frequently recurring picture is that of a Coulomb potential like Eq. (1) with indications of the interaction between charges in a dielectricum. Gregg and Hanna [17] suggest that the strong interaction in excitons is caused by the small dielectric constant in typical OPVs ( $\epsilon \approx 4$ ), in contrast with the free electron-hole pairs in inorganic semiconductors ( $\epsilon \approx 15$ ). In 2004, Gregg et al. [18] put this even stronger: “Thus, increasing  $\epsilon$  . . . leads to a greater average distance between the charges.” But there is also a warning: “Finally,  $\epsilon$  is a bulk quantity and is valid only over distances of many lattice spacings; . . .” Unfortunately, in following papers, this warning is absent, and in the recent review of Clarke and Durrant [2] the dielectric constant is still a very important parameter, and the Onsager model, or more recently developed versions [19–23] of it, is still the main [1] operative theory. [24] In all these works the expected effect of the dielectric constant (or the permittivity) comes from model calculations based on the Onsager model.

Lately, an increasing number of studies have been reported in which microscopic descriptions are used for specific systems [25–31]. However, also there the importance of the dielectric constant is (often) mentioned [1,24,25].

## 2. Dielectric or not?

Recently Van Duijnen and Swart reported a Discrete Reaction Field (DRF) study on  $\text{Si}_n$ -clusters [33] ( $n$  ranging from 3 to ~5000) in which they arrived from first principles at the experimental dielectric constant for the larger clusters ( $n = 1750, 4950$ ). In a correct treatment of the many-body polarisation in an arbitrary



**Figure 1.** Effective atomic polarisability of C and Si in C/Si<sub>4950</sub>-clusters in their experimental (diamond) structures as a function of the distance to the centre.

collection of point charges and polarisabilities, the induced dipole  $\mu_p$  in the polarisable point  $p$  is determined by the local field, *i.e.*, the sum of the external field and the fields,  $t_{pq}$ , of all dipoles induced elsewhere:

$$\mu_p = \alpha_p [E_p^0 + \sum_{q \neq p} t_{pq} \mu_q] \quad (4)$$

$E^0$  consists of any applied field plus the field of any charge distribution in the system [34–39]. The dipole–dipole interaction tensors  $t_{pq}$  in Eq. (4) contain only geometric parameters.

Hence, it is through the mutual orientation and distances that the polarisable particles respond differently in various (local) structures, which in the end makes the results sometimes counter-intuitive and cannot be caught in the simple form of Eq. (1).

In DRF, the two-particle interactions are damped at short distances in order to avoid too large and unphysical results [34,40]. The electric potentials, fields and field gradients of charges are damped in a consistent way and the damped fields and dipole–dipole tensors are the derivatives of the potential and the field, respectively [32]. Eq. (4) for the many-particle problem can be put into matrix form:

$$\mathbf{M} = \mathbf{B}\mathbf{E}^0 = [\mathbf{A}^{-1} - \mathbf{T}]^{-1} \mathbf{E}^0 \quad (5)$$

in which  $\mathbf{M}$  is the vector of (self-consistent) induced dipoles,  $\mathbf{E}^0$  the vector of the initial field,  $\mathbf{A}$  the block-diagonal matrix of the (vacuum) polarisabilities, and  $\mathbf{T}$  the (off-diagonal) interaction tensors. Hence,  $\mathbf{B}$  is a normal (but many-body) polarisability thus leading to an induction energy:

$$U_{\text{ind}} = -\frac{1}{2} \mathbf{E}^0 \mathbf{B} \mathbf{E}^0 \quad (6)$$

By applying unit fields in  $x$ -,  $y$ - and  $z$ -directions, the *effective* mean polarisabilities are obtained from Eq. (5). We note here that the  $\mathbf{T}$ -blocks in the condensed phases generally lead to effective local polarisabilities that are *smaller* than the vacuum values [33].

Reversely, by fitting Eq. (5) to (experimental or calculated) molecular polarisabilities, the vacuum, or ‘free-atom’ polarisabilities  $\{\alpha_p\}$  are obtained. With these (‘input’) parameters the polarisabilities of molecules – not belonging to the learning sets – are calculated from Eq. (5) with experimental accuracy [41]. Typically, each ‘free’ atomic polarisability is independent of its ‘chemical environment’: the latter is in all cases absorbed in the  $\mathbf{T}$ -blocks of  $\mathbf{B}$ .

In Figure 1, the average (per atom) mean polarisabilities of the atoms of a cluster consisting of 4950 atoms of carbon and silicon in

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