

Non-conventional screening of the Coulomb interaction in low-dimensional and finite-size systems

J. VAN DEN BRINK^{1,2} and G. A. SAWATZKY²

¹ *Department of Applied Physics, University of Twente
P.O. Box 217, 7500 AE Enschede, The Netherlands*

² *Laboratory of Applied and Solid State Physics, Materials Science Center,
University of Groningen - Nijenborgh 4, 9747 AG Groningen, The Netherlands*

(received 2 February 2000; accepted in final form 20 March 2000)

PACS. 31.25.Qm – Electron-correlation calculations for polyatomic molecules.

PACS. 71.20.Tx – Fullerenes and related materials; intercalation compounds.

PACS. 71.27.+a – Strongly correlated electron systems; heavy fermions.

Abstract. – We study the screening of the Coulomb interaction in non-polar systems by polarizable atoms. We show that in low dimensions and small finite-size systems this screening deviates strongly from that conventionally assumed. In fact in one dimension the short-range interaction is strongly screened and the long-range interaction is anti-screened thereby strongly reducing the gradient of the Coulomb interaction and therefore the correlation effects. We argue that this effect explains the success of mean-field single-particle theories for large molecules.

A very old and perhaps the most intellectually challenging problem in condensed-matter physics concerns the role of the Coulomb interaction in determining the physical properties of solids. In wide-bandwidth semiconductors the Coulomb interactions give rise to Wannier excitonic states; in narrow band materials the Coulomb interactions can result in insulating and usually magnetic ground states as in the 3D transition metal oxides, rare earths, or actinides, and very strongly bound excitons well inside the conductivity gap. In molecular solids as in many organic, C₆₀, and polymeric materials the Coulomb interaction gives rise again to deep Frenkel excitons. The very wide field of strongly correlated materials involving the above examples as well as the high- T_c cuprates, the colossal magnetoresistance materials, spin Peierls systems, Kondo impurity and Kondo lattice systems owe their longstanding interest to the fact that the Coulomb interactions involving the valence electrons are not sufficiently screened in the solid to allow the use of one-electron-like theories. On the other hand, those who are convinced of the importance of the many-body problem in solids are also continually confronted with the success of one-electron-like band theories and mean-field-like quantum chemistry methods even for systems for which one may have thought that a single Slater determinant description of the ground state and the low energy scale excited states could not possibly be applicable. Realizing that it is really the spacial gradient of the Coulomb interaction which plays the decisive role for correlation effects, we have taken another look at how the Coulomb interactions are screened in the solid concentrating especially on the range of the

interaction and on the effects of dimensionality and finite size. In doing so we have come across some rather interesting properties which have led us to the conclusion that the standard uniform dielectric theories usually used to describe screening in solids have some very important shortcomings especially in lower dimensions even to the extent that long-range interactions in solids may in fact be enhanced rather than screened. This of course could have very important consequences leading to a larger, rather than smaller, range of Coulomb interactions in some solids, bringing us closer to the limiting case of a constant interaction for which of course one-electron theory or mean-field theory would be exact. In this letter we present the findings of a study of screening of the Coulomb interaction in 1-, 2- and 3-dimensional structures composed of polarizable atoms. Within this model we treat the range of the interactions exactly. We first describe how such a medium screens even the on-site Coulomb interaction and then go on to look at the longer-range interactions finding the strange result that in a 1-dimensional row of atoms the short-range interactions are screened and the longer-range interactions are anti-screened. We discuss in detail why this happens and what the shortcomings are of the commonly used uniform dielectric theory for screening.

The most commonly used screening theories in solids replace the discrete atomic lattice by a uniform medium and use a self-consistent mean-field treatment of a q -dependent dielectric function, or in ionic insulators the Clausius-Mossotti (CM) derivation of a dielectric constant in terms of the atomic polarizabilities, resulting in a screened potential of the form $V(q) = V_0(q)/\epsilon(q)$. In this relation local-field corrections are neglected as the screened potential is assumed to be a function of only the distance between charges and all effects due to the crystal structure are neglected. Further, one often neglects the q -dependence of ϵ so that $V(r) = V_0(r)/\epsilon$, *i.e.* it simply reduced in magnitude. Well-known exceptions to this are the Friedel oscillations in an electron gas and the exponential Debye-Huckel or Thomas-Fermi screening in semiconductors and insulators. In any case one generally assumes, and finds, that the long-range Coulomb interactions are, if anything, more strongly screened than the short-range ones. This assumption is in fact the basis for the Hubbard model much used to describe strongly correlated systems in which only the on-site Coulomb interaction is explicitly included.

There are several basic problems with the uniform dielectric theory for the screening of Coulomb interaction between the valence electrons, especially in narrow-band systems. First of all, it is difficult to describe the screening of the Coulomb interaction between two electrons on the same atom. At first glance one might assume that, since there is no polarizable medium between these two electrons, the interaction would not be screened in the solid. If this were the case then the Hubbard U would retain its bare atomic value which is typically 20 eV and virtually all materials would be Mott-Hubbard insulators. The second problem is that a 3D uniform medium theory cannot describe properly the Coulomb interactions in a low-dimensional system. It is rather easy to imagine that in such cases the local-field correction will be very important and may even dominate because the field lines are not restricted to be inside the medium. This was investigated some time ago by Keldysh [1], who still used a uniform theory but restricted the polarizable medium to a thin two-dimensional layer. He showed that the long-range Coulomb interaction is considerably larger than in a 3D solid, resulting in a larger exciton binding energy. We would expect that in one dimension the effects would be even more dramatic. We study this general problem with a model based on polarizable atoms in a 1D, 2D or 3D lattice and in finite-size systems like C_{60} or small atomic clusters. We look both at how the on-site Coulomb interaction is screened in the solid and what the distance dependence looks like.

The linear response of the atoms to an electric field induces a dipole moment $\mathbf{p}(\mathbf{r}_i)$ on an atom on site \mathbf{r}_i proportional to the local field $\mathbf{F}(\mathbf{r}_i)$: $\mathbf{p}(\mathbf{r}_i) = \alpha_i \mathbf{F}(\mathbf{r}_i)$, where α is the

atomic polarizability. The energy is lowered due to the induced dipole moment by $\Delta E_i = -\frac{1}{2}\alpha_i |\mathbf{F}(\mathbf{r}_i)|^2$. Using this, the screened value of the Hubbard U can be obtained [2]. The mathematical description of the microscopic response of such a system of point-dipoles to external fields was developed by Mott and Littleton [3] and has proved to be a powerful method to calculate, for instance, local-field corrections for point-charge defects [4] and (surface) core-level shifts in photoemission [5]. Consider two electrons, one at the origin of our coordinate system and one at \mathbf{R} . The aim is to calculate the electrostatic energy V of the system as a function of \mathbf{R} . The total energy consists of four parts: the potential energy due to the monopole-monopole, monopole-dipole and dipole-dipole interactions plus the energy stored in the induced dipoles [4]. The total electrostatic energy is given by

$$V(\mathbf{R}) = \frac{e^2}{R} - \frac{1}{2} \sum_i \mathbf{d}_i \cdot \mathbf{p}_i \equiv \frac{e^2}{R} - 2E_p(\mathbf{R}), \quad (1)$$

where \mathbf{d}_i is the total external monopole field and \mathbf{p}_i the induced dipole moment at site i . The bare Coulomb repulsion is reduced by the polarization energy $2E_p(\mathbf{R})$, as defined in the last part of equation (1). Now the dipole moment at each site has to be determined. The induced dipole moment is proportional to the local field on the atom, leading to

$$\begin{aligned} \mathbf{p}(\mathbf{r}) = & \alpha e \mathbf{r} / |\mathbf{r}|^3 + \alpha e (\mathbf{r} - \mathbf{R}) / |\mathbf{r} - \mathbf{R}|^3 + \\ & + \alpha \sum_{\mathbf{l}, \mathbf{l} \neq 0} \frac{1}{|\mathbf{l}|^5} \{ [3\mathbf{p}(\mathbf{r} + \mathbf{l}) \cdot \mathbf{l}] \mathbf{l} - |\mathbf{l}|^2 \mathbf{p}(\mathbf{r} + \mathbf{l}) \}. \end{aligned} \quad (2)$$

This equality for N atoms results in DN coupled equations for $\mathbf{p}(\mathbf{r}_i)$, where D is the dimensionality of the system. The matrix representation of eq. (2) in Cartesian coordinates is

$$p_i^\mu = \alpha_i d_i^\mu + \sum_\gamma \sum_{j, j \neq i} M_{ij}^{\mu\gamma} p_j^\gamma, \quad \text{with } \mu, \gamma = x, y, z. \quad (3)$$

The elements of the matrix that represents the dipole-dipole interactions are given by

$$M_{ij}^{\mu\gamma} = \alpha_i (3l_{ij}^\mu l_{ij}^\gamma |l_{ij}|^{-5} - |l_{ij}|^{-3} \delta_{\mu\gamma}), \quad (4)$$

where $l_{ij} = \mathbf{l}_i - \mathbf{l}_j$ is the vector connecting the two dipoles. The solution of this set of equations gives the exact effective potential for the electrons. In some cases the equation can be solved in wave vector space [6], but in general the less cumbersome method is to solve the equation numerically in real space.

It is easy to show that the formulation above reduces to the CM relation $\frac{\epsilon-1}{\epsilon+2} = 4\pi\alpha/3$, when a) the dipole-dipole interaction is averaged over and b) the lattice is treated as a continuum. An obvious improvement up on the CM result is to evaluate the lattice sum in eq. (1) exactly. Within this partial continuum limit of this model, where dipole-dipole interactions are taken into account on the CM level, values for the polarization energy and the effective on-site Coulomb interaction U that compare well with experiment can be obtained [2].

If one wants to take the dipole-dipole interaction into account without using the CM relation, one has to solve the matrix equation (3). Only a limited number of equations can be solved numerically. If the symmetries of the problem are taken into account, the number of equations can be substantially reduced. In this way one can easily treat a 1D string of $\sim 10^4$ atoms. To obtain convergence for a 3D system, we subdivide the lattice into four regions. For atoms within a sphere of radius r_0 around each electron a system of equations is set up. Around these spheres a sphere with radius r_1 is constructed for which the partial continuum

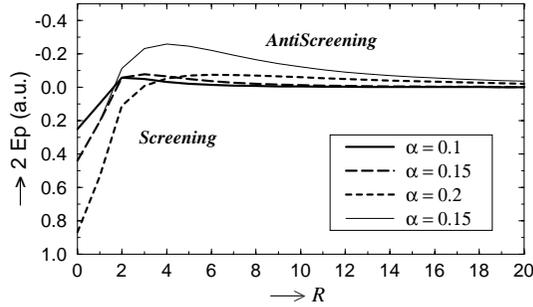


Fig. 1 – The polarization energy $2E_p$ as a function of separation (in units of the lattice spacing) between the electrons in one dimension. Positive values of E_p represent screening and negative values anti-screening. The thin line represents $2RE_p$ for $\alpha = 0.15$.

result is used. The rest of the crystal is treated as a continuum. To obtain a relative accuracy better than 1%, typically an r_0 of five lattice spacings and an r_1 twice as large, is sufficient. We find that for a 3D cubic system the exact effective potential deviates no more than around 10% from the CM expression, except if the charges are at the same site, as has been discussed before [2].

The situation is very different for a system where the dipoles and electrons are confined to a plane (2D system) or a line (1D system), a geometry that can be encountered in a material where a chain of polarizable atoms is embedded in a non-polarizing matrix. As the system is an object in the 3D real space, the bare Coulomb interaction between the two electrons is inversely proportional to the distance between the charges. For a 1D system the polarization energy is calculated exactly and shown in fig. 1. At very short distances (till about 2 lattice spacings) the Coulomb interaction is screened. When the separation between the charges is larger, however, the Coulomb interaction is *anti-screened*: the induced polarization results in an increased repulsion between the two charges. This behavior is markedly different from the CM result. In fact it is the opposite to the usually assumed behavior that long-range interactions are screened and short-range interactions are not or only weakly screened. In the figure also RE_p as a function of distance is shown. If a dielectric constant ϵ can be defined,

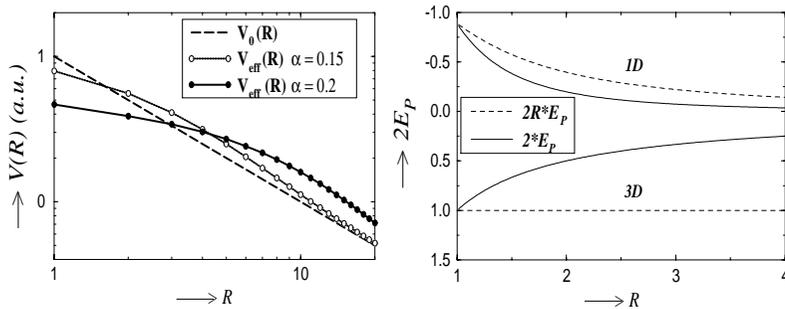


Fig. 2 – Left: effective Coulomb potential in a 1D system with $\alpha = 0$, $\alpha = 0.15$ and $\alpha = 0.2$ on a log-log scale. The dashed straight line represents the unscreened Coulomb interaction. Right: polarization energy $2E_p$ as a function of separation between the electrons in one and three dimensions in the continuum limit. In the 1D system $r_0 = 0.5$. Distances are in units of the lattice spacing.

then $2RE_p = 1 - 1/\epsilon$. From the figure it can be seen that $2RE_p \rightarrow 0$ when $R \rightarrow \infty$, so that at large distances $\epsilon \rightarrow 1$ and the Coulomb potential is unscreened. As a consequence, the effective potential between the charges is flattened out. At short distances the bare Coulomb potential is large, but also the polarization energy is large; see fig. 2. At intermediate distances the Coulomb potential decays, but the polarization enhances the repulsive interaction so that in the end the effective potential decays much slower than $1/R$. In a 2D system an analogue situation is encountered.

Why is this result so different from what one expects on the basis of the CM relation? If the distance between the electrons is large, the lattice can be treated as a continuum and the lattice sum can be replaced by an integral. In the low-dimensional systems the outcome of the integral does not only depend on the distance between the two electrons, but also on the range of integration. In order to make the integral convergent we have to assume a sphere around each electron with radius r_0 , in which the polarizability is zero.

In fig. 2 the outcome of the continuum integral as a function of separation between the electrons is plotted. For clarity the proportionality constants are set to unity. The behavior for the 3D system is as expected: the polarization energy is positive and proportional to $1/|R|$. In the 1D system, however, the polarization energy is negative, implying that screening effects *increase* the repulsion between the charges. This explains the anti-screening of the Coulomb repulsion at large distances found in the exact calculation. The figure also shows that the polarization energy decays faster than $1/|R|$ at large distances. This can be expected since in 1D and 2D the integration is not over a volume, but rather over a line and a surface, respectively. The consequence is that in low-dimensional systems the Coulomb potential is unscreened at large distances. The exact calculation for the 1D system shows that the screening energy is positive at short distances. This can be understood by considering the limiting case where the two charges are on the same atom. The polarization energy associated with a single electron is a constant times the square of its electrical field cF^2 , so that the total polarization energy of a system where two electrons are infinitely far apart is $2cF^2$. If the two electrons are on the same site, the total field is $2F$ resulting in a polarization energy of $4cF^2$. So the screening energy related to two charges at the same site is always larger than the screening energy of two charges far apart, explaining why at short distances the Coulomb potential is always screened. We now turn to a few finite-size systems. For a C_{60} molecule we can model the screening by assuming that on each carbon site a dipole moment can be induced due to two excess charges on the molecule. The effective Coulomb repulsion between these two charges is calculated by the method described above. The results for the C_{60} molecule is shown in the inset of fig. 3. Whereas the bare Coulomb repulsion depends strongly on the distance between the charges (ranging from ~ 13.5 to ~ 2 eV), screening tends to flatten the effective interaction (ranging from ~ 6 to ~ 3 eV). This is again due to the fact that at short distances the Coulomb interaction is screened and at large distances anti-screened, as in the 1D case. This behavior compares well with what has been found by Gunnarsson *et al.* [7] and Lof *et al.* [8]. The variation of the effective potential at short length scales is caused by the geometry of the C_{60} molecule.

In fig. 3 the results for benzene and two linear benzologues, naphthalene and a polymer consisting of 200 benzene rings, is shown. The carbon-carbon distances and carbon polarizability are taken from ref. [9]. The Coulomb potential for larger molecules is screened more effectively because more atoms participate in the screening process. For all these systems, however, the variation of the effective Coulomb potential over the molecule is drastically reduced by screening effects. For distant neighbors there is anti-screening, since the introduction of an electron on the molecules moves screening charge to the opposite side of the molecule causing the screening clouds of the two charges to interfere destructively. Obviously this makes the

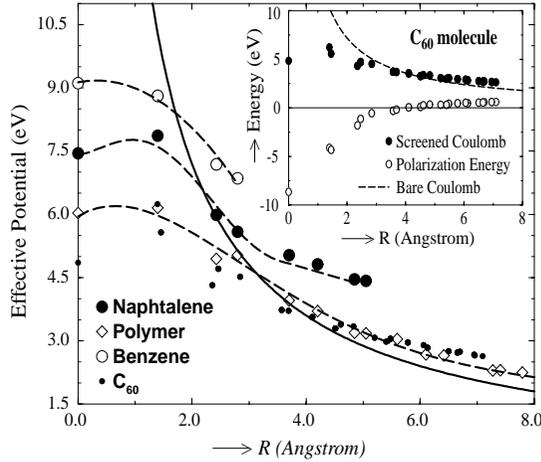


Fig. 3 – Effective Coulomb interaction in different organic molecules. The full line represents the bare Coulomb repulsion, dashed lines are guides for the eye. Inset: effective Coulomb interaction as a function of the separation of two electrons on a C_{60} molecule. The carbon polarizability is 0.56 \AA^3 .

C_{60} molecule and the linear benzologues less correlated: the electrons move in a relatively uniform effective potential. It is also interesting that the on-site and nearest-neighbor Coulomb interactions in these systems are almost equal, which really makes a Hubbard-like description very questionable [10]. This explains why one-particle theories that do not take correlation effects fully into account work so well for large organic molecules.

The systems we have studied here are all isolated or embedded in a non-polarizable medium. Interesting questions arise when systems are in polarizing surroundings like organic molecules in solution or polymers on a metallic or semiconducting substrate. Although we have not studied this in detail, it is fairly obvious that our conclusions can be strongly modified by the surrounding medium. For example, putting a molecule on a surface of a metal strongly affects both the short- and long-range Coulomb interactions as recently demonstrated for C_{60} on a silver surface [11]. A present topic of research involves using the surrounding medium to tune correlation effects and properties of solids and molecules.

In conclusion, we considered a point-dipole model to account for the screening of the Coulomb repulsion in non-polar insulators. For three-dimensional systems the deviations from the Clausius-Mossotti result for the inter-site screened Coulomb interaction are small, but in one- and two-dimensional systems only local-field effects contribute to the screening. At large distances the Coulomb interaction is unscreened and in 1D at intermediate distances the Coulomb interaction is even anti-screened. Applying the dipole-screening model to finite-size systems like large organic molecules, we showed that the effective Coulomb interaction is only weakly dependent on the distance between the electrons. So correlation effects are drastically reduced, explaining the success of one-particle, molecular-orbital theory for large molecules.

We thank L. HEDIN and O. GUNNARSSON for useful discussions. This work was supported by the Nederlandse Stichtingen FOM and SON, both supported by NWO. JvdB acknowledges with appreciation the support by the Alexander von Humboldt-Stiftung, Germany.

REFERENCES

- [1] KELDYSH L. V., *JETP Lett.*, **29** (1979) 659.
- [2] J. VAN DEN BRINK *et al.*, *Phys. Rev. Lett.*, **75** (1995) 4658; **76** (1996) 2826.
- [3] MOTT N. F. and LITTLETON M. J., *Trans. Faraday Soc.*, **34** (1938) 485.
- [4] WANG J. C., *Phys. Rev. B*, **22** (1980) 2725.
- [5] DE BOER D. K. G., HAAS C. and SAWATZKY G. A., *Phys. Rev. B*, **29** (1984) 4401; ROTENBERG E. *et al.*, *Phys. Rev. B*, **54** (1996) R5279.
- [6] MAHAN G. D., *Phys. Rev. B*, **21** (1980) 4791.
- [7] GUNNARSSON O. and ZWICKNAGEL G., *Phys. Rev. Lett.*, **69** (1992) 957.
- [8] LOF R. W. *et al.*, *J. Electron. Spectrosc. Relat. Phenom.*, **72** (1995) 83.
- [9] SILINSH E. A., *Organic Molecular Crystals* (Springer-Verlag, Berlin) 1980.
- [10] VAN DEN BRINK J., EDER R. and SAWATZKY G. A., *Europhys. Lett.*, **37** (1997) 471.
- [11] HESPER R., TJENG L. H. and SAWATZKY G. A., *Europhys. Lett.*, **40** (1997) 177.