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1993 J. Phys.: Condens. Matter 5 8047

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Screening effects in C₆₀ solids

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Received 8 June 1993, in final form 13 August 1993

Abstract. The dielectric function for solid C₆₀ is calculated within local-density-functional theory. The screened Coulomb interaction shows a remarkable orientation and position dependence. Inter-molecular screening is stronger than intra-molecular screening and screening increases with inter-molecular separation. Some of the inequivalent on-site atomic screened Coulomb integrals are comparable to the nearest-neighbour terms and the second-nearest-neighbour terms are smaller than the third-nearest-neighbour terms. The screened on-site molecular Coulomb integral U_0 is found to be ~ 2.1 eV and the local multiplet splitting for three electrons in the t_{1u} is ~ 0.12 eV, suggesting that electrons in the derived band should be highly correlated.

1. Introduction

Since the discovery of C₆₀ [1], but especially after the discovery that C₆₀ doped with certain alkali metals [2] becomes superconducting, there has been a wide-ranging experimental and theoretical effort to understand the microscopic properties of C₆₀ and its derivatives. Indications are that many-body properties play an important role in the behaviour of C₆₀ solids [3–5]. Lof *et al* [5], for example, suggested, on the basis of results of KVV C₆₀ Auger spectroscopy, that doped C₆₀ should be considered a strongly correlated system and predicted that K₃C₆₀ is a half-filled Mott–Hubbard insulator. It is therefore of great interest to understand the screened electron–electron interaction in C₆₀ systems. Gunnarson *et al* [6] investigated the screening in C₆₀ using a simple model within the random phase approximation (RPA). Screening properties of C₆₀ systems were also studied by Gonzalez *et al* [7] using a continuum model. Experimentally derived values for the macroscopic dielectric function $\epsilon_0 = 4.6$ [20] and 3.6 [21], indicate that screening is relatively weak in solid C₆₀. These results, however, do not yield any information on the rich local structure of screening in fullerenes.

The screened interaction has a remarkably rich structure as a function of position and orientation, a property which is probably related to the hollow structure of the C₆₀ molecules. Of great interest are the screened Coulomb integrals, which give an indication of the importance of correlation effects. The screened on-site molecular Coulomb integral is large at 2.1 eV, similar to the value estimated by Lof *et al* [5], and the local multiplet splitting of the t_{1u} lowest unoccupied molecular orbital LUMO, for an additional three electrons per C₆₀ molecule, is ~ 0.12 eV, comparable to the width (~ 0.4 eV [8]) of the corresponding band derived from the molecular t_{1u} orbitals. This suggests that correlation effects must be taken into account in any realistic investigation of the microscopic electronic structure of C₆₀.

In this paper an investigation of the screening properties of FCC T_h³ C₆₀ (figure 1) is reported. In section 2 the background to the dielectric screening function and computational

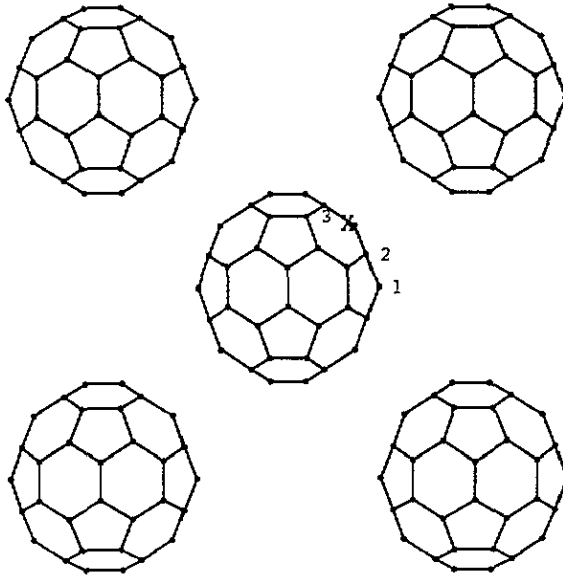


Figure 1. Atomic positions for nearest-neighbours of solid FCC T_h^3 C60 projected on the (100) plane.

details are discussed. In section 3, results are presented and in section 4, a summary and conclusions are given.

2. Model

Within density functional theory the electronic contribution to the static dielectric function can be calculated exactly [9]:

$$\epsilon^{-1}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r}, \mathbf{r}') + \int d\mathbf{r} v(\mathbf{r}, \mathbf{r}'') \chi(\mathbf{r}'', \mathbf{r}') \quad (1)$$

with v the Coulomb interaction and where the polarizability χ is given by

$$\chi = (1 - \chi_0 v - \chi_0 K_{xc})^{-1} \chi_0. \quad (2)$$

The Fourier transform of the independent particle polarizability χ_0 for a semiconductor, can be expressed as

$$\chi_{GG'}(\mathbf{q}) = 4 \sum_{v,c} \frac{\langle \psi_v | \exp[-i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}] | \psi_c \rangle \langle \psi_c | \exp[i(\mathbf{q} + \mathbf{G}') \cdot \mathbf{r}] | \psi_v \rangle}{\epsilon_v - \epsilon_c} \quad (3)$$

where ψ_v and ψ_c are the valence and conduction band wave functions and ϵ_v and ϵ_c the corresponding eigenenergies. The exchange–correlation contribution is included via K_{xc} , which, in the local density approximation (LDA) is given by

$$K_{xc}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 E_{xc}}{\delta \rho(\mathbf{r}) \delta(\mathbf{r}')} = \left. \frac{dV_{xc}}{d\rho} \right|_{\rho(\mathbf{r})} \delta(\mathbf{r} - \mathbf{r}'). \quad (4)$$

Here E_{xc} is the local exchange–correlation energy, and V_{xc} the corresponding exchange–correlation potential.

Setting $K_{xc} = 0$ in equation (2) reduces the related functions to the RPA in which no account is taken of exchange–correlation in the polarizability of the system of electrons.

The expression for the inverse dielectric function in equation (1) is appropriate for the interaction between two 'test charges', i.e. charges external to the system of electrons that are polarized by the presence of the 'test charges'. If the system is probed by the electrons themselves, the appropriate function is given by

$$\epsilon^{-1} = 1 + (v + K_{xc})\chi. \quad (5)$$

In this paper only equation (1) will be considered. In other words, only the effect of the polarization associated with the electrons in the neutral system will be included and the 'test charges' used to probe the system are considered to be external to the closed shell C_{60} molecules. In doped C_{60} , such as K_3C_{60} , each C_{60} molecule becomes charged. If these 'excess' electrons are considered to be external to the neutral closed shell C_{60} molecules, the appropriate dielectric function that determines the effective interaction between them is given by equation (1).

The average, or macroscopic, response of the system, defined as

$$\epsilon_M(\mathbf{q} + \mathbf{G}) = 1/\epsilon_{GG}^{-1}(\mathbf{q}) \quad (6)$$

is determined by the diagonal elements of ϵ^{-1} , not ϵ [10]. In particular, the macroscopic dielectric function $\epsilon_0 = \lim_{q \rightarrow 0} \epsilon_M(\mathbf{q})$, since it is determined by the inverse of ϵ , depends on the non-diagonal elements of ϵ , or on the so-called local fields [18]. An example of the importance of local fields is the difference between ϵ_0 and $\epsilon_{00}^{-1}(0)$. In C_{60} $\epsilon_{00}^{-1}(0) \simeq 0.5\epsilon_0$, indicative of the important role that local fields play in this system.

In solid C_{60} the molecules are arranged at the lattice sites of an FCC structure. The FCC $T_h^3 C_{60}$ structure is chosen since this is the structure with the highest symmetry consistent with an FCC arrangement of the C_{60} molecules. It is unlikely that the orientational ordering of C_{60} molecules will significantly influence the screening properties of the system and the higher symmetry has considerable computational advantages. In this calculation the lattice parameter used is 14.2 Å and the nearest-neighbour atomic bond lengths are 1.369 Å (between pentagons) and 1.453 Å (on pentagons) [16, 17]. The solid FCC $T_h^3 C_{60}$ is a semiconductor with a calculated direct bandgap of ~ 1.8 eV. In the present calculation the electronic structure was determined within the LDF [11] using the non-local pseudopotential of Bachelet *et al* [12] and the exchange-correlation function of Ceperley and Alder [13] as parametrized by Perdew and Zunger [14]. Basis functions were constructed from a contracted Gaussian basis for the 2s and 2p C wave functions. Up to ~ 1200 reciprocal lattice vectors were used in the calculation of the dielectric matrix and derived functions. This gave results which are converged to, in the worst cases, $\sim 3\%$, but in most cases the convergence was within 1%.

3. Results

The long-wavelength limit of the calculated dielectric function $\epsilon_{00}(0) = 4.84$. This value agrees very well with that calculated by Ching *et al* [15] using a similar approach. The macroscopic dielectric function ϵ_0 , calculated as 2.33, is only $\sim 50\%$ of $\epsilon_{00}(0)$, an indication that local field effects are important in C_{60} . As a comparison it is worth noting that local field effects in more conventional tetrahedrally bonded semiconductors such as Si and Ge are usually only 10–20% in ϵ_0 [18].

Experimentally derived values of ϵ_0 , 4.6 [20] and 3.6 [21], are closer in value to $\epsilon_{00}(0)$ than to ϵ_0 . The calculated value is therefore only $\sim 50\%$ of the experimental value. This is also in contrast with calculations for conventional semiconductors [18] where the calculated values tend to be higher than the experimental values. The inclusion of

exchange–correlation effects usually increases the calculated macroscopic response [18, 19]. In the present calculation for C_{60} , exchange–correlation increases ϵ_0 by about 1%. The discrepancy between experimental and calculated results suggests that the lattice contribution to polarization in C_{60} may be of considerable importance. Inclusion of continuum states and an improved set of basis functions may increase the value of ϵ_0 , but it is highly unlikely that the increase will be of the order of 50%.

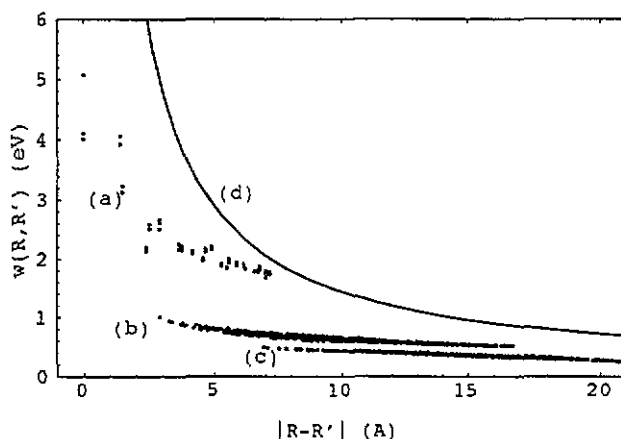


Figure 2. Screened interaction $w(\mathbf{R}, \mathbf{R}')$ as a function of separation: points a, the same molecule; points b, two test electrons on nearest-neighbours; points c, two test electrons on next-nearest-neighbours; curves d, bare Coulomb interaction.

In order to investigate the effects of screening on the electron–electron interaction, the screened interaction between two test electrons constrained to move in the vicinity of the surfaces of C_{60} molecules was calculated. In figure 2 the function

$$w(\mathbf{R}, \mathbf{R}') = \int d\mathbf{r} d\mathbf{r}' \phi_{\pi}^2(\mathbf{r} - \mathbf{R}) \epsilon^{-1} v(\mathbf{r}, \mathbf{r}') \phi_{\pi}^2(\mathbf{r}' - \mathbf{R}') \quad (7)$$

is plotted as a function of the separation $|\mathbf{R} - \mathbf{R}'|$ for a range of separations. Here $\epsilon^{-1} v(\mathbf{r}, \mathbf{r}')$ is the screened Coulomb interaction and the ϕ_{π} are the radially directed p orbitals centred at atomic sites \mathbf{R} . There are three clearly defined regions labelled (a), (b) and (c). The points (a) refer to \mathbf{R} and \mathbf{R}' on the same C_{60} cluster, (b) illustrates the behaviour for \mathbf{R} and \mathbf{R}' located on nearest-neighbour clusters and (c) refers to \mathbf{R} and \mathbf{R}' located on second-nearest-neighbours. The most striking feature is that the screening is highly dependent on orientation. The inter-molecular screening is much better than the intra-molecular screening, at least in the regions where the atomic separations overlap, and consistently improves with inter-molecular separation. If $\epsilon_{GG}^{-1}(q)$ were diagonal, $w(\mathbf{R}, \mathbf{R}')$ would only have depended on $|\mathbf{R} - \mathbf{R}'|$. The strong dependence on orientation once more demonstrates the importance of local fields. It is interesting to note that for intra-molecular screening, the screened third-nearest atomic neighbour interaction is less than the screened fourth- and fifth-nearest atomic neighbour interactions. The difference is a few tenths of an electronvolt and is unlikely to have great physical significance for effects that depend on electrons delocalized on an atomic scale, such as the screened Coulomb interaction of electrons in the lowest states above the gap.

More noteworthy is the observation that screening decreases as a function of separation for each of the three regions illustrated in figure 2. This property is shown more graphically in figure 3 where the ratio of bare-to-screened interaction, a function that essentially

describes the local screening, is plotted as a function of atomic separation. A curious property of the intra-molecular screening is that it decreases to almost zero as two test charges are taken to opposite sides of the molecule. This trend was also observed by Gunnarson *et al* [6] in a model calculation, but they found a more pronounced effect for an isolated molecule in that anti-screening occurs across the molecule. In the current calculation it was found that if only terms diagonal in the basis functions localized on the atomic sites are included in the expression for the polarizability, an approximation similar to that made by Gunnarson *et al* [6], anti-screening across the C_{60} molecules is generated. This suggests that anti-screening is a model-dependent feature, but does not rule out the possibility that it may occur in an isolated molecule.

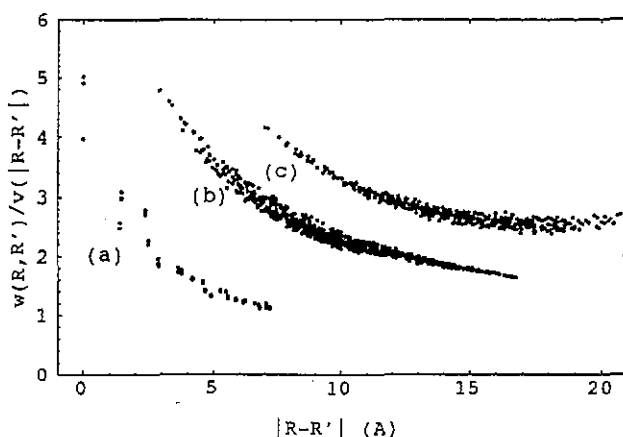


Figure 3. Ratio $v(\mathbf{R}, \mathbf{R}')/w(\mathbf{R}, \mathbf{R}')$, for bare-to-screened interaction as a function of separation. The points (a), (b) and (c) are defined as in Figure 2.

The reduction to almost zero of the intra-molecular screening as a function of separation can be understood by investigating the screening charge. In figure 4 a spherical cross section of the induced charge at a radius of 3.8 \AA is shown for an electron situated at position X (also indicated in figure 1) on the enclosing sphere (radius 3.5 \AA). Most of the action occurs near the test-charge. The induced charge has a complicated distribution, but, as expected, there is a region in the vicinity of the test-charge where the pseudo-charge is depleted, and to compensate for this, there are regions where the pseudo-charge is enhanced, but these are also relatively close to the test charge. The contribution to the effective interaction at r due to the induced charge $\rho_{\text{ind}}(\mathbf{r})$, the screening potential $v_{\text{sc}}(\mathbf{r})$, can be expressed as

$$v_{\text{sc}}(\mathbf{r}) = \int d\mathbf{r}'' \frac{\rho_{\text{ind}}(\mathbf{r}'')}{|\mathbf{r} - \mathbf{r}''|}. \quad (8)$$

Since the induced charge must approximately integrate to zero for each molecule, the contribution to the screened interaction from neighbouring molecules can at most be dipolar. The major contribution to the screening potential therefore originates from the local cluster. If we ignore neighbours and only consider the intra-molecular contribution, then since $\int d\mathbf{r} \rho_{\text{ind}}(\mathbf{r}) \rightarrow 0$ for a integration volume small in comparison with the volume of the cluster (figure 4), the induced charge contributes little to the screening potential as $|\mathbf{r} - \mathbf{r}'|$, the separation between two test charges, approaches the diameter of the molecule and $v_{\text{sc}} \rightarrow v_e$ at the same time. For further neighbours the interaction is more complicated, but a measure of the process just discussed is still likely to play a role.

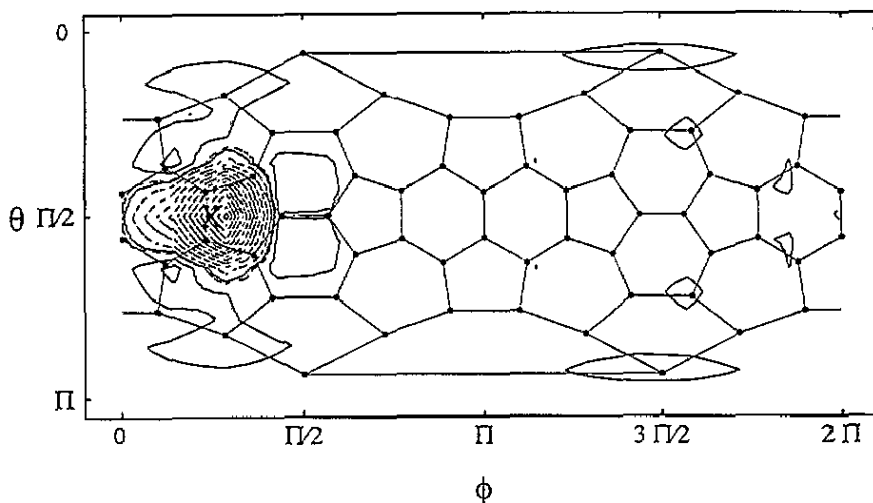


Figure 4. Cross section of the induced charge at a radius of 3.8 Å for an electron situated at position X on the enclosing sphere (see also figure 1). Broken contours indicate pseudo-charge depletion and full contours pseudo-charge enhancement. The contour interval is eight electrons per unit cell.

The exchange–correlation contribution to the screened interaction is most pronounced for the on-site screened Coulomb interaction. There are three inequivalent atomic sites in the FCC $T_h^3 C_{60}$ structure, marked 1, 2 and 3 in figure 1. The on-site term, $w(\mathbf{R}, \mathbf{R})$, takes on three different values for the three inequivalent sites, with two terms, those for sites 2 and 3, almost equal to the first-nearest-neighbour interaction. This is different from the RPA calculation where the on-site terms are almost equal at ~ 6.2 eV. The exchange–correlation term changes the on-site terms from the corresponding RPA values by $\sim 24\%$ for 1 and $\sim 50\%$ for 2 and 3, and the scattering in these terms becomes much more pronounced. For more distant neighbours the difference between the RPA value for $w(\mathbf{R}, \mathbf{R}')$ and the full screened interaction is less than 3%, although the variation can be positive or negative. The fact that some atomic on-site terms are almost equal in value to first-neighbour terms makes it imperative that models for C_{60} systems take this into account.

The importance of the molecular nearest- and even next-nearest-neighbour Coulomb repulsion, since they are of the same order as the molecular on-site term, is also evident from figure 2. This suggests that simple Hubbard models for the doped solid C_{60} , which only include a molecular on-site repulsion, may not be adequate. In such systems the effective on-site Coulomb interaction is reduced to the difference between the intra-molecular Coulomb repulsion and the next-nearest-neighbour one. This would result in an underestimate of the electronic correlation effects in the doped system.

3.1. Screened Coulomb integrals and multiplet splitting

The LUMO for an isolated C_{60} molecule has t_{1u} symmetry. Within the LDF this set of orbitals gives rise to an isolated band of states with a width of ~ 0.47 eV [8]. The centre of this band is separated from the centre of the highest occupied band by ~ 1.8 eV. The next band, derived from t_{1g} molecular orbitals, is centred ~ 0.65 eV above the first and also has a width of ~ 0.5 eV. The molecular orbitals that give rise to these bands are derived almost exclusively ($> 98\%$) from ϕ_π orbitals centred at the atomic sites. In the alkali metal doped

systems, such as $K_n C_{60}$ ($n = 1, 2, \dots, 6$), the alkali metal atoms are ionized and the 'excess' electrons are largely localized on the C_{60} molecules.

Locally two electrons in t_{1u} split into ${}^3T_{1g}$, 1H_g and 1A_g states in an icosahedral environment, i.e. for the isolated molecule. The energies associated with these correlated wave functions can be expressed in terms of two Coulomb integrals: a monopolar term U_0 and a dipolar term U_2 . The corresponding associated energies are $U_0 - \frac{5}{3}U_2$ and $U_0 + \frac{1}{3}U_2$ and $U_0 + \frac{10}{3}U_2$ gives a total multiplet splitting of $5U_2$. Three electrons in the t_{1u} level split into 4A_u , 2H_u and ${}^2T_{1u}$ states with energies $3U_0 - 5U_2$, $3U_0 - 2U_2$ and $3U_0$ respectively. In this instance the total multiplet splitting is also $5U_2$. In the present calculation the screened values of U_0 and U_2 are 2.12 eV and 0.024 eV respectively. This must be contrasted with the bare Coulomb values of 4.12 eV and 0.10 eV. The effective dipolar term is reduced by a factor of about four whereas the monopolar term is only halved by the response of the system. This is a consequence of the highly anisotropic nature of the screened interaction. The multiplet splitting for the bare and screened parameters are 0.5 eV and 0.12 eV respectively. Thus even the splitting for the screened interaction is of the order of the bandwidth in the solid. This and the high value of U_0 clearly suggest that the excess electrons on the C_{60} molecules in the doped C_{60} system are highly correlated.

A number of estimates for U_0 and U_2 have appeared in the literature. Lof *et al* [5] estimated $U_0 = \pm 1.6$ eV from Auger spectrum results. The well localized behaviour of the induced charge density around the test charge in figure 4 suggests that the core hole created on one of the C atoms in the molecule in Auger measurements will also give rise to such localized behaviour. The Coulomb repulsion estimated by Lof *et al* [5] should thus have more of an atomic-site than molecular-site nature. A direct comparison between the calculated molecular-site repulsion and the value derived from Auger spectroscopy is therefore not justified. Another estimate was made by Antropov *et al* [4] who argued, using a simple model, that U_0 should be between 0.8 and 1.3 eV.

In extrapolating the results of the present calculation to a doped C_{60} system a few cautionary remarks are necessary. In the first place the influence of the dopant ions on the band structure is not taken into account. Secondly, the excess electrons are treated as external to the C_{60} molecules and the polarization taken into account is due only to the electrons associated with the neutral system. Since the expression for the polarizability involves a *summation* over the eigenstates of the system the first approximation is unlikely to be accurate. The excess electrons occupy extended states in the doped system and, at least for lightly doped systems, even though the contribution is metallic in nature, the contribution to the polarizability is likely to be small. To be consistent when using the excess electrons to probe the system, while including a contribution from these to the polarizability, demands the use of equation (5), i.e. including K_{xc} in the pre-factor of the polarizability. It is not clear what the combined effect of these latter two contributions will be. However, the approximation for K_{xc} [14] used in the present calculation is negative, and since the bare Coulomb interaction is positive it follows that $(v + K_{xc}) < v$. The increase in polarizability due to a contribution from the excess electrons will therefore be countered by this. Consequently the approximations used may not be unreasonable.

4. Summary and conclusions

In summary, screening in FCC $T_h^3 C_{60}$ was investigated in the LDA. The screened Coulomb interaction was found to be highly position and orientation dependent with the implication that local field effects are important. Screening decreases with separation, but there is a significant difference between intra- and inter-molecular screening. Intra-molecular

screening is weaker than inter-molecular screening in the regions where inter-atomic separations overlap, while inter-molecular screening shows a relative increase with inter-molecular separation. For nearest-neighbour inter-molecular screening the reduction varies between ~ 5 and ~ 2 and for next-nearest neighbours it varies between ~ 4 and ~ 3 . The net effect is that the inter-molecular screened interaction is almost independent of atomic separation for given neighbours, in contrast to the bare interaction. For example, the bare Coulomb interaction varies between ~ 4.8 and ~ 0.8 eV for atomic separation on nearest molecular neighbours, whereas the screened interaction only varies by ~ 0.3 eV. The on-site atomic screened Coulomb integral is reduced by ~ 5 or ~ 4 depending on the type of site. As a consequence the better screened on-site terms are approximately equal to the first neighbour terms. Across a molecule the screening is reduced to almost zero.

The on-site molecular screened Coulomb integral is large, 2.1 eV, while the dipolar term is better screened at 0.12 eV. These values clearly suggest that the excess electrons on the C_{60} molecules in a doped C_{60} system should be highly correlated.

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