Field-doping of C\textsubscript{60} crystals: Polarization and Stark splitting

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(Dated: November 2, 2018)

PACS numbers: 73.61.Wp,73.90.+f,74.70.Wz

We investigate the possibility of doping C\textsubscript{60} crystals by applying a strong electric field. For an accurate description of a C\textsubscript{60} field-effect device we introduce a multipole expansion of the field, the response of the C\textsubscript{60} molecules, and the Stark splitting of the molecular levels. The relevant response coefficients and splittings are calculated \textit{ab initio} for several high symmetry orientations. Using a group theoretic analysis we extend these results to arbitrary orientations of the C\textsubscript{60} molecules with respect to the external field. We find that, surprisingly, for the highest occupied (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively, the two leading multipole components lift the degeneracy of the molecular level in the same way. Moreover the relative signs of the splittings turn out to be such that the splittings add up when the external field induces charge into the respective level. That means that when charge carriers are put into a level, its electronic structure should be quite different from that of the alkali-doped fullerenes.

I. MOTIVATION

The proposal of doping C\textsubscript{60} crystals in a field-effect device (FET) and the possibility of metallic conduction and even superconductivity in such devices had raised widespread interest. While the revelation of dishonest data handling in some cases led to a severe damping of the initial enthusiasm, fundamental aspects of field effect doping remains a timely and interesting problem. For field-effect transistors made with self-assembled monolayers handling in some cases spread interest. While the revelation of dishonest data even superconductivity in such devices had raised wide-
The response of a molecule to external multipole fields is a fundamental concept in the study of molecular interactions. In this context, the external field, whether electric or magnetic, can induce changes in the molecular charge distribution, leading to a splitting of the molecular levels. This effect is particularly pronounced in systems with high symmetry, such as fullerene C$_{60}$, where the molecular levels are determined by the induced charge and the polarization for arbitrary configurations.

### II. RESPONSE OF A C$_{60}$ MOLECULE

To determine the response of a C$_{60}$ molecule to external multipole fields, we have performed all-electron density functional calculations using Gaussian-orbitals. The basis set comprises 5s4p3d for carbon and we use the Perdew-Burke-Ernzerhof functional. In our calculations, we apply an external multipole field and study the multipole moments of the charge density and the splitting of the molecular levels as a function of the strength of the external field. To take advantage of the molecule’s symmetry, we consider multipole fields with the z-axis along the 2-, 3-, and 5-fold axis of the molecule. As these axes are each contained in a mirror plane, which we chose to be the x-z-plane, we can treat the molecule as having symmetry group C$_{2v}$, C$_{3v}$, and C$_{5v}$, respectively. Applying external multipole fields with $l > 0$, this symmetry is maintained if the fields are proportional to the real part of the spherical harmonic Y$_{lm}$, where $m$ is an integer multiple of the order ($n=2, 3, 5$) of the symmetry axis. Likewise, the response of the charge density will only have multipole components proportional to Re(Y$_{lm}$), with $m$ an integer multiple of $n$. Calculations were done for such symmetry conserving multipole fields up to $l=6$. For the 3-fold axis oriented along z, we have, in addition, calculated the response to external fields proportional to Im(Y$_{5,3}$), Im(Y$_{5,3}$), and Im(Y$_{6,0}$), i.e., with a symmetry lowered to C$_{5}$. As we are interested in the linear response,
we have considered small multipole fields and made sure that the calculated response of the charge density is indeed proportional to the strength of the external field. We find that the linear response of a C60 molecule is very similar to that of a metallic sphere of radius 4.4 Å. This effective sphere radius shows a slight increase with \( l \), In addition there are weak off-diagonal terms. To judge the accuracy of our calculation, we have checked how well the selection rules, that are not already imposed by the \( C_{nv} \) symmetry, are fulfilled for these off-diagonal terms.

From the calculated response, we have determined the irreducible linear response coefficients, which will be given in the next section.

In addition to polarizing the molecule, the external field also splits the degenerate molecular levels of the C60 molecule. As the unperturbed molecular orbitals have a definite parity, for a multipole field with odd \( l \) there will be no first-order splitting — the quadratic Stark effect. On the other hand, a multipole field with even \( l \) can couple states of like parity, so in that case the splitting is linear. This is shown in figure 2. In section IV it will be demonstrated how the splitting of the HOMO- and LUMO-orbitals that were calculated for high-symmetry geometries can be extended by group theory to arbitrary orientations of the molecule relative to the external multipole field.

All calculations have been performed for the equilibrium geometry of the unperturbed, neutral C60 molecule. To estimate the effect of an external field on the shape of the molecule, we have relaxed the structure in the presence of homogeneous external fields of up to 1 V/Å. We find only small changes (up to about 0.005 Å) in the lengths of the bonds (1.40 Å for the short and 1.45 Å for the long bonds). Likewise, the polarizability changes by less than 1.5%.

Finally, we have calculated the total energy of the isolated C60 ion as a function of its charge \( q \) (spin unpolarized calculation with relaxed geometries) and extracted the second order term \( 1/2 U_0 q^2 \). To compare with previous calculations we find for the polarizability (multipole field with \( l = 1 \)) of the neutral molecule \( \alpha = 9.3 \) bohr\(^3\)/atom, and \( U_0 = 3.2 \) eV.

**III. IRREDUCIBLE RESPONSE PARAMETERS**

The polarizability \( \alpha \) of a molecule describes the linear dependence of the induced dipole moment \( \mathbf{p} = \alpha \mathbf{E} \) on the applied electric field \( \mathbf{E} \). For a multipole expansion, \( \alpha \) becomes a matrix \( \alpha_{l_1 m_1, l_2 m_2} \) describing the response to all multipole fields. To fix the notation (which follows Ref. 11) we briefly review the definition of the multipole response matrix.

The solutions of the Laplace equation \( \nabla^2 V(r) = 0 \) are given by

\[
V(r) = V^e + V^i = \sum_{lm} V_{lm} R_{lm}^e(r) + Q_{lm} I_{lm}(r),
\]

where the two terms denote the external potential \( (V^e) \), and the induced potential \( (V^i) \) due to a charge distribution \( \rho \) located around \( r = 0 \). Note that both, the Laplace equation as well as the expansion of \( V(r) \) into multipole only holds for \( r \) which lie outside the charge distribution. We have introduced the regular and irregular spherical harmonics

\[
R_{lm}(r) = r^l \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\Omega),
\]

\[
I_{lm}(r) = \frac{1}{r^{l+1}} \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\Omega).
\]

Special cases for the regular spherical harmonics are \( R_{00} = 1 \) and \( R_{10} = z \), hence, the external field, \( V_0 = V_0 \) corresponds to a constant shift, and \( V_{10} = -E_z \) is the \( z \)-component of the electric field. For the irregular spherical harmonics we have \( I_{00} = 1/r \) and \( I_{10} = z/r^3 \), thus for the induced potential, \( Q_{00} = q \) gives the monopole charge while \( Q_{10} = p_z \) is the dipole moment. Generally, the coefficients \( Q_{lm} \) are the multipole moments of the
charge distribution $\rho$

$$Q_{lm} = \int d^3r \rho(r) R_{lm}(r).$$  \hfill (4)

Decomposing the charge distribution $\rho = \rho_0 + \Delta \rho$ into the unperturbed charge density and the change in the charge density due to the external potential, we obtain a decomposition of the multipole moments $Q_{lm} = Q_{0lm}^0 + \Delta Q_{lm}$. Within linear response, the coefficients $\Delta Q_{lm}$ of the induced multipole moments depend linearly on the coefficients $V_{lm}$ of the external potential, which defines the linear-response matrix $\alpha_{lm12m2}$:

$$\Delta Q_{l1m_1} = - \sum_{l_2m_2} \alpha_{lm12m_2} V_{l_2m_2},$$  \hfill (5)

where the sign takes into account that the induced fields oppose the external fields. Then $\alpha_{lm12m2}$ gives the dipolar response tensor, while $\alpha_{0000}$ is the self-capacitance $U_0$.

The interaction energy of the molecule with the external potential is $E_{\text{ext}} = \int d^3r \rho(r) V^e(r)$, which, using the previous definitions, reduces to

$$E_{\text{ext}} = \sum_{lm} V_{lm} Q_{lm}^*.$$  \hfill (6)

Therefore, $V_{lm}$ and $Q_{lm}$ are pairs of conjugate variables and the total energy of the molecule as a function of the external field is given by

$$E_{\text{tot}} = -\frac{1}{2} \sum_{l_2m_2} \alpha_{lm12m_2} V_{l_1m_1} V_{l_2m_2}^* + \sum_{lm} V_{lm} (Q_{lm}^0)^*.$$  \hfill (7)

Since this is a quadratic form, we see that the matrix $\alpha$ is hermitian. We can make $\alpha$ real and symmetric by unitarily transforming to a real basis (using $\sqrt{2} \Re(Y_{lm})$ and $\sqrt{2} \Im(Y_{lm})$ instead of $Y_{lm}$ and $Y_{l,-m}$ for $m \neq 0$).

The structure of the response matrix $\alpha$ depends on the symmetry of the molecule. For a metallic sphere of radius $R$ the response is isotropic, i.e., $\alpha$ is diagonal in the basis of the spherical harmonics: $\alpha_{lm12m2} = \delta_{l_1l_2} \delta_{m_1m_2} R^{2l_1+1}$. Lowering the symmetry to icosahedral, $I_h$, introduces some anisotropy. To understand the response matrix for $C_{60}$ we have to consider how the irreducible representations (IR) of the rotation group $SO(3)$ split into IRs of the $I_h$ (see table I). An external multipole field of angular momentum $l$ can only give rise to a response with angular momentum $l'$, if both IRs of the $SO(3)$ contain a common IR of the $I_h$. In particular, because of parity, fields with even (odd) $l$ can only give rise to responses with even (odd) $l'$. Furthermore, as the irreducible representations with $l \leq 2$ are also irreducible with respect to the $I_h$, for $l \leq 2$ we have $\alpha_{lm12m2} = \alpha_{l12l2m2}$. Thus, restricting the multipole expansion to $l \leq 2$, the response of $C_{60}$ is isotropic, with $\alpha_0 \approx 8.1 \text{ bohr}^6$, $\alpha_1 \approx 556 \text{ bohr}^8$, and $\alpha_2 \approx 44100 \text{ bohr}^{10}$.

| $l$ | $I_h$ |
| --- | --- |
| 0 | $A_g$ |
| 1 | $T_{1u}$ |
| 2 | $H_g$ |
| 3 | $G_u \oplus T_{2u}$ |
| 4 | $G_u \oplus H_g$ |
| 5 | $T_{1u} \oplus T_{2u} \oplus H_u$ |
| 6 | $A_g \oplus T_{1g} \oplus G_u \oplus H_g$ |

TABLE I: Decomposition of the irreducible representations (IR) of the rotation group $SO(3)$ into the IR of the icosahedral group $I_h \subset SO(3)$.

For $l > 2$ the space spanned by the spherical harmonics $Y_{lm}$ is no longer irreducible with respect to the $I_h$. Thus we need to find linear combinations of the spherical harmonics that span the irreducible representations of the icosahedral group. We call them $Y_{lzk}$ where $l$ and $z$ denote the IR of the $SO(3)$ and $I_h$, respectively, while the index $k$ labels the functions within an irreducible representation of the $I_h$. If in the decomposition an IR $x$ should occur several times, we would have to introduce an additional multiplicity label. However, as can be seen from table II up to $l = 6$ each IR appears at most once. We therefore suppress the multiplicity label here. Explicit expressions for the basis functions $Y_{lzk}$ can, e.g., be found in Ref. 12 chapter 16, or Ref. 13 table 4.2.

In the new basis, the matrix $\alpha$ is built of blocks of diagonal matrices

$$\alpha_{l1x1k_1,l2x2k_2} = \alpha_{l1l2}(x_1) \delta_{x_1x_2} \delta_{k_1k_2},$$  \hfill (8)

where $\alpha_{l1l2}(x_1)$ constitute the minimal set of parameters, and, $\alpha$ being real symmetric, $\alpha_{l1l2}(x_1) = \alpha_{l2l1}(x_1)$. The matrix elements of $\alpha$ were calculated up to $l = 6$ using the results of the density functional calculations described in section II. The $\alpha_{l1x1k_1}(x_1)$ are listed in table II. From this minimal set of independent parameters we can determine the response for arbitrary orientations of the $C_{60}$ molecule relative to the external multipole field. An example of how to do this is given in appendix A. The practical advantage of this procedure is clear: We only need to perform density functional calculations for a number of highly symmetric configurations, for which the numerical effort is much reduced. Using group theory the response for arbitrary configurations can then be determined from these special cases.

Note that the group theoretical approach presented in this section is particularly elegant in the case of a neutral molecule which has icosahedral symmetry. Upon charging, orbitals become partially filled and the symmetry is reduced which leads to a higher number of irreducible response coefficients. Furthermore, the symmetry of a charged molecule depends on how the additional charge arranges in the degenerate orbitals. This is a subtle question in the case of an isolated $C_{60}$ molecule and involves Jahn-Teller effects and Coulomb interaction in competition. In the present work we restrict the analysis to neutral molecules.
The change of the ground state energy upon charging of the molecule is given by the linear change $\Delta V^{\text{eff}}(r)$ in the external potential $V_e$ and, using the notation of the previous section, can be written as

$$\Delta V^{\text{eff}}(r) = \sum_{l zk} V_{l zk} f^l_{zk}(r) + O[V_e^2], \quad (10)$$

where $f^l_{zk}(r)$ are partner functions of the IR $x$ of $I_h$. Note that $f^l_{zk}$ contains spherical harmonics $Y_{l2k}$ with all $l'$ allowed by table I. The coupling of the degenerate levels is given by the matrix elements of $\Delta V^{\text{eff}}$ with respect to the eigenstates of the unperturbed molecule which are denoted by $|n lk\rangle$, where $n$ is the quantum number differentiating between orbitals with the same IR $x$. In this context, the functions $f^l_{zk}$ play the role of tensor operators of $I_h$ and the Wigner-Eckart theorem can be used to write the matrix elements as

$$\langle n_{2x2k'}|\Delta V^{\text{eff}}|n_{1x1k}\rangle = \sum_{l zk} V_{l zk} t_{\lambda}(n_{1x1}, n_{2x2}; l x) C^k_{k'k}(\lambda; x_{12} x_{11}), \quad (11)$$

The coefficients $C^k_{k'k}(\lambda; x_{12} x_{11}; x)$ denote the 3jm symbols (or Clebsch-Gordan coefficients) of $I_h$ and are entirely determined by the icosahedral symmetry. In the present work they were taken from Ref. 12 and are discussed in detail in appendix B. In order for $C^k_{k'k}(\lambda; x_{21} x_{11})$ to be non-zero, the IR $x$ needs to be present in the decomposition of $x_2$ in $x_1$. If $x_2$ occurs more than once in a $x_1 \otimes x_2$ then the multiplicity index $\lambda$ is required. From this selection rule follows again that even potentials couple linearly whereas odd potentials couple only in second order (quadratic Stark effect). Finally, the factors $t_{\lambda}(n_{1x1}, n_{2x2}; l x)$ are the coupling constants which constitute the minimal set of parameters describing the level splitting.

We analyze in more detail the level splitting of the LUMO ($x = T_{1u}$) and HOMO ($x = H_g$) for $l = 1$ and $l = 2$ external potentials which correspond to an electric field and a quadrupole potential. We will see in Section V that these two multipoles are dominant in the case of a charged C$_{60}$ layer exposed to an electric field. Within the icosahedral symmetry $I_h$, the two potentials form partners for the IR $T_{1u}$ and $H_g$ respectively (see table I). Details of the calculation are given in appendix B. The coupling constant derived from the level splitting calculated by DFT are given in table III. In the case of the odd $l = 1$ potential, only second-order coupling to closest-by orbitals was considered ($T_{1g}$ for the LUMO, $H_g$ and $G_g$ for the HOMO, see figure 3), which, however, as shown below, gives very satisfactory results. For the splitting of the HOMO under the $l = 2$ ($x = H_g$) potential, there are two coupling constants because $H_g$ occurs twice in the product $H_u \otimes H_u = A_g \oplus T_{1g} \oplus T_{2g} \oplus 2G_g \oplus 2H_g$. In appendix B the coupling matrix $H'_{1u}(H'_{1u})$ describing the level splitting of the LUMO (HOMO), due to an applied $(lm) = (10)$ and $(lm) = (20)$ potential along an
The LUMO and HOMO subspace respectively and de-

tions of the

are quite remarkable, as they imply that the contribu-

tion of splitting is given by the sum of the

levels have almost the same radial dependence because of the

TABLE III: Coupling constants

t_{\alpha}(x_1 x_2; l) as defined by equation [11] (indices n_1, n_2, l are dropped) among the

energy levels near the Fermi energy. The coupling constants are
given in units of eV (7 bohr)^2 e^(-1) where l = 1 for x = T_{1u}
and l = 2 for x = H_g. The negative sign of the coefficients
is due to the negative charge of the electrons. Note that the

coupling constants t(H_u H_g; T_{1u}) and t(H_u G_g; T_{1u}) are equal

up to the third digit which is due to fact that the H_g and G_g

levels have almost the same radial dependence because of the

arbitrary direction of the molecule, is calculated using

perturbation theory. To a very good approximation, the

result can be cast into the form

H'_{T_{1u}}(\theta) = \left( V_{T_{1u}}^2 c_1 + V_{20} c_2 \right) C_{T_{1u}}(\theta), \quad (12)

H'_{H_g}(\theta) = \left( V_{H_g}^2 d_1 + V_{20} d_2 \right) C_{H_g}(\theta), \quad (13)

where c_1, c_2, d_1 and d_2 are constants depending on the

coupling constants of table [III] and the energies given in

figure [X] C_{T_{1u}}(\theta) and C_{H_g}(\theta) are matrices within

the LUMO and HOMO subspace respectively and depend on the angle \theta between the z-direction of the

potential and the 5-fold axis of the molecule. (For more details see appendix [III].) In figure [Y] and figure [Z] the splitting of the LUMO and HOMO is

shown using the previous relations along with the points calculated by DFT. The group-theoretical fit is very satis-

factory. Note that the splitting of the LUMO is independent of the orientation of the molecule when only coupling among the LUMO or to the T_{1g} is considered

(see appendix [III]). Furthermore, relations [12] and [13]

are quite remarkable, as they imply that the contribu-

tions of the l = 1 and l = 2 potential lift the degeneracy

of the molecular levels in the same way, and thus the

total splitting is given by the sum of the l = 1 and l = 2

splittings.

V. MOLECULES IN A LAYER

In this section a simple model of a C_{60} FET is con-

sidered. As mentioned above a FET can be understood as
capacitance where one plate is the gate and the other plate is the material (here C_{60}) which is investigated. An

analysis of this device, in particular the calculation of the

charge distribution, was done in a previous work. It was found, that the charge concentrates on the first layer in

the high doping regime. In what follows, we take this as

a motivation to consider a single layer of C_{60} molecules

which acts as a plate of a capacitance. We use the re-

sponse of a neutral molecule (table [III]) to describe the electrostatic behavior of the molecules in the layer. The
doped charge is taken care of by adding a monopole on

every site. The molecules are then exposed to the electric

field arising from the gate as well as the monopole fields

of the neighboring molecules. In order to simplify the
calculation, we assume a perfect lattice, either square, for

the (001), or triangular, for the (111) plane of the fcc lat-
tice formed by the C_{60} molecules in the bulk. In order for

the sites to be equivalent we neglect the non-spherically

symmetric part of the response of the C_{60}-molecule and

use the averaged response given by

$$
\alpha_{l_1 m_1 l_2 m_2}^{\text{sym}} = \delta_{l_1 l_2} \delta_{m_1 m_2} \sum_{x k} \frac{\alpha_{x k i} l_1 x k}{2l_1 1 + 1},
$$

(14)

where the sum is taken over all components of the l_1

subspace. Since the response of C_{60} for multipoles l \leq 2

is isotropic (cf. section [III]), this averaging is exact for

l = 1, 2.

Because of translational invariance, the total potential

is given by

$$
V_{\text{tot}}(\mathbf{r}) = V^e(\mathbf{r}) + \sum_{\mathbf{R}_l} V^i(\mathbf{r} - \mathbf{R}_l),
$$

(15)

where the sum is taken over all lattice sites \mathbf{R}_l. At a

given site, say \mathbf{R}_l = 0, the total potential can also be de-

composed as $V_{\text{tot}}(\mathbf{r}) = V^e(\mathbf{r}) + V^i(\mathbf{r})$ where the screened
potential $V^{\text{scr}}(r) = V^\alpha(r) + \sum_{\mathbf{R}_i \neq 0} V^i (r - \mathbf{R}_i)$ contains the external potential $V^\alpha(r)$ as well as the sum of all induced potentials of the other molecules. This sum depends linearly on the induced potential $V^i$ and, hence, the coefficients of $V^{\text{scr}}$ are given by

$$V^{\text{scr}}_{l_1, m_1} = V_{l_1, m_1} + \sum_{l_2 m_2} \beta_{l_1 m_1 l_2 m_2} Q_{l_2 m_2}. \quad (16)$$

The matrix $\beta$ is entirely given by geometry and discussed in appendix A. On the other hand, the screened potential $V^{\text{scr}}$ induces a potential $\Delta V^i$ as given in equation (19). Therefore the total induced potential $V^i = V^{\text{bare}} + \Delta V^i$ is

$$Q_{l_1 m_1} = Q^{\text{bare}}_{l_1 m_1} + \sum_{l_2 m_2} \alpha_{l_1 m_1 l_2 m_2} V^{\text{scr}}_{l_2 m_2}. \quad (17)$$

Equations (16) and (17) can be combined by eliminating the coefficients $Q_{l m}$ which yields

$$V^{\text{scr}}_{l_1 m_1} = \sum_{l_2 m_2} [1 + \beta \alpha]^{-1} Q_0^{l_1 m_1 l_2 m_2} V^\text{bare}_{l_2 m_2}, \quad (18)$$

$$V^\text{bare}_{l_1 m_1} = V_{l_1 m_1} + \sum_{l_2 m_2} \beta_{l_1 m_1 l_2 m_2} Q_0^{l_2 m_2}, \quad (19)$$

where the $V^\text{bare}_{l_1 m_1}$ describes the bare potential arising from the external potential (the electric field of the gate) and intrinsic moments of the molecules (the induced charge, i.e. monopoles). The square (triangular) lattice in the presence of the electric field has the rotational symmetry $C_{4v}$ ($C_{6v}$). As a consequence, only components with these symmetries are non-zero and therefore they are given by $\Re(Y_{lm})$ with $m$ a multiple of 4 (6). Using relation (18) and (19) the screened potential can be calculated. The non-zero components entering (19) are the monopole charge $Q_0$ and electric field $V_{10} = -E_{\text{Gate}}$. As the FET is overall neutral $E_{\text{Gate}} = -2\pi q/\text{A}_{\text{mol}}$ with $A_{(001)} = a^2/2$ for the square lattice and $A_{(111)} = \sqrt{3}a^2/4$ for the triangular lattice. The results are given in table IV and graphically depicted in figure 6. The components $(l m) = (10), (20)$ are most dominant and higher ones are at least one order of magnitude smaller. This justifies a posteriori the assumption of spherical symmetry because (14) is exact for $(l m) = (10), (20)$. From figure 6 it can be seen that the electric field is efficiently screened within the layer. Note that decrease of the electric field yields negative sign of $V_{20}$ in table IV.

![FIG. 5: Splitting of the HOMO for an $(l m) = (10)$ and $(l m) = (20)$ potential. See figure 4 for more details. In this plot the similarity of the splitting resulting from the different potentials (cf. eqn. (15)).](image)

![FIG. 6: Screened potential $V^{\text{scr}}$ across the layer with the parameters from Tab IV for the square and triangular lattice. The gate is assumed to be on the left. The lower lines correspond to a cut through the center of the molecule whereas the upper lines are along half-circles with the radius of the molecule (7 bohr $\approx 3.7$ Å).](image)

| $(l m)$ | square $Q^\text{bare}_{l m}$ | $Q^\text{scr}_{l m}$ | triangular $Q^\text{bare}_{l m}$ | $Q^\text{scr}_{l m}$ |
|--------|-----------------------------|----------------------|-------------------------------|----------------------|
| 10     | 0.862                      | 0.499                | 0.996                         | 0.530                |
| 20     | −0.230                     | −0.189               | −0.280                        | −0.219               |
| 30     | 0                          | 0.039                | 0                             | 0.053                |
| 40     | 0.0133                     | 0.0030               | 0.0177                        | 0.0015               |
| 4e4    | 0.0174                     | 0.0097               | -                             | -                    |

TABLE IV: Components of the bare and screened potential for the square and triangular lattice with $a/\sqrt{2} = 10$ Å. The coefficients are in units of $q/(7 \text{ bohr})^{1/2}$, where $q$ is the charge per $C_{60}$ molecule. Note that 7 bohr $\approx 3.7$ Å is about the radius of the $C_{60}$ molecule.
VI. SPLITTING IN SELF-CONSISTENT MULTipoLE FIELD

We are now in the position to estimate the effect of the external field on the electronic structure of the C\textsubscript{60} molecules in the monolayer that carries charge. To do so we have performed density functional calculations for a molecule in the self-consistent multipole fields as determined in the previous section (cf. table [V]). Figure 7 shows the splitting of the molecular levels in the self-consistent field for a (001) monolayer, where the molecule is oriented with one of its two-fold axes pointing in the direction of the external field. The maximum energy difference between split states is given in table V and compared to the result from the perturbative formula (12) and (13), which is in good agreement for |q| ≤ 2. As figure 8 demonstrates, similar results are obtained for other geometries. Qualitatively, the results are also in agreement with an approximative tight-binding calculation published earlier in Ref. 17. As expected we find that the stronger the external field, i.e., the larger the induced charge, the stronger the splitting. We notice also a pronounced asymmetry in the splitting: when the monolayer is charged with electrons the splitting is different from when it is charged with holes. Again, the reason is parity: Because of parity an external homogeneous field, and more generally any multipole potential with l = 0, leads to a quadratic Stark effect. Hence, for odd l the splitting is independent of the sign of the field. For l even, however, the levels split already in first order (linear Stark effect), so the splitting changes sign with the external field. Thus the asymmetry originates from the multipoles with even l. Moreover, because of the first-order versus second-order effect, even though the largest even multipole (20) is significantly smaller than the largest odd multipole (the screened external field), it contributes considerably to the splitting.

We have seen in section IV that for the HOMO and LUMO of C\textsubscript{60} the splittings caused by (10) and (20) multipole potentials are essentially additive (cf. equation 11). Thus we expect them to add up for one sign of the external field, while they should compensate for the opposite sign. In fact, for electron doping the splittings of the HOMO seem to almost perfectly cancel, while upon hole doping the splitting of the HOMO is essentially doubled compared to the splitting caused by the screened homogeneous field alone. Thus for the HOMO, the splittings happen to add up for an external field that induces charge carriers into that orbital — a situation that is particularly unfavorable for hole doping. For the LUMO the situation is similar: For an external field that induces electrons in the LUMO the splitting is enhanced. So it turns out that the contributions of the higher multipoles conspire to enhance the splitting of the orbital that carries the induced charge. For both, HOMO and LUMO, the splitting becomes comparable to the respective band width for a field that corresponds to about two charge carriers per molecule.

| q | HOMO DFT DFT | HOMO Pert. Pert. |
|---|---|---|
| -2e | 0.151 | 0.207 |
| -1e | 0.151 | 0.207 |
| 0 | 0 | 0 |
| 1e | 0.006 | 0.002 |
| 2e | 0.057 | 0.097 |
| 3e | 0.151 | 0.207 |

TABLE V: Maximum energy difference (in eV) between split HOMO and LUMO states, respectively, as a function of doping q of the square lattice. 2nd and 4th column are the DFT results from figure 7. 3rd and 5th column are calculated by perturbation theory as described in section IV.

The calculations reported above have been performed for an uncharged molecule. Considering instead the splitting for a molecule that carries the proper induced charge, the splittings are substantially reduced. This is easily understood: Due to the splitting, the electrons will shift only the lowest of the split levels. But since the interaction between electrons in the same orbital is larger than the interaction of electrons in different orbitals, the occupied levels will be shifted upwards, compared to the levels that were left empty — thereby reducing the splitting. We are, however, not interested in the splitting per se, but in the effect of the splitting on the band structure of a monolayer. Thus allowing electrons only in the energetically lowest levels would mean that in the lattice, the electrons are not allowed to hop to energetically higher ones of the split levels. This implies that the original band structure would already be separated into a set of bands originating from occupied, and another set of bands originating from the empty orbitals. To eliminate the undesired differences in the interaction between electrons in the split orbitals, we therefore work with the splittings obtained for a neutral molecule.

To estimate the effect of the Stark splitting on the density of states (DOS), we have performed tight-binding calculations for the (001) monolayer (square lattice), assuming the unidirectional structure (two-fold axis of the molecules pointing in the direction of the external field). The basis for the tight-binding Hamiltonian and the hopping matrix elements were taken from the parametrization given in Ref. 18. The splittings shown in figure 7 were then used to derive an on-site coupling between the different orbitals. In the case of the LUMO, the on-site coupling is diagonal and reduces to orbital dependent on-site energies. The DOS for the LUMO (T\textsubscript{1\textsubscript{u}}) and the HOMO (H\textsubscript{u}) bands calculated with this model for different charging are shown in figure 9 and 10, respectively. We find that already for an induced charge of one carrier per molecule the change with respect to the unperturbed DOS is sizable. For q = -2 one of the T\textsubscript{1\textsubscript{u}}-bands is already completely separated from the other two. Also the HOMO density of states shows for q = 2 hardly any resemblance to the original DOS, and for q = 3 also the H\textsubscript{u}-bands fall into two groups. We thus conclude that...
FIG. 7: Splitting of the molecular levels of a $\text{C}_{60}$ molecule in the self-consistent multipole potential ($l \leq 2$) for a (001) monolayer (square lattice) in a homogeneous external field as a function of the induced charge. The molecule is oriented such that one of its two-fold axis points in the direction of the external field (perpendicular to the monolayer). The top panel shows the positions of the split (from bottom to top) $H_g$, $G_g$, $H_u$, $T_{1u}$, and $T_{1g}$ levels. The bottom gives the splitting of the $H_u$ (HOMO) and $T_{1u}$ (LUMO) levels relative to their respective center of gravity.

Beyond filling $|q| = 2$ the electronic structure is distorted so much compared to the unperturbed monolayer that one can no longer speak of doping.

The calculation of the density of states in a minimal tight-binding basis involves, of course, approximations: First, in the lattice, not only hopping between LUMO (HOMO) levels is allowed, but also hopping via energetically close-by levels. An orbital at $\Delta \varepsilon$ away will give a contribution to the hopping of about $t^2/\Delta \varepsilon$, where $t$ is the hopping matrix element from the orbital, that we consider explicitly, to the orbital at $\Delta \varepsilon$. The influence of this effect on the hopping between molecules was studied in Ref. [18] and changes of the order of 5% were found. More importantly, due to the deformation of the molecular orbitals in the field, the hopping matrix elements between the HOMO or LUMO orbitals will change. For a simple estimate, we have performed tight-binding calculations of a $\text{C}_{60}$ molecule in an external homogeneous field and determined the average hopping matrix element between the $t_{1u}$-orbitals following the approach of Ref. [19]. We find that the change in the hopping matrix elements depends strongly on the orientation of the molecules. Typical changes are of the order of 10–20%.

VII. CONCLUSIONS

We have analyzed the changes in the electronic structure of a $\text{C}_{60}$ monolayer in which charge carriers are induced by the application of an external homogeneous electric field. We find that the effective field seen by each molecule in the monolayer is strongly screened, but that there are additional higher multipole potentials. Although these components are considerably weaker than the screened homogeneous field, for even $l$, they give a significant contribution to the level splitting as they are of first order. In addition the $l = 1$ (homogeneous field) and $l = 2$ potentials split the HOMO and LUMO in almost the same way, so the splittings they produce add up or counteract, depending on the sign of the external field. For both, the HOMO and the LUMO, the signs turn out to be such, that the splitting is enhanced when the charge
is induced in the respective level. Thus the level that carries the field-induced charge is strongly changed by the effective field — a particularly unfavorable situation if one wants to achieve doping, i.e., filling of a level without substantially changing its electronic structure.

There are, of course, some effects that have been neglected in our analysis: The polarizability of C$_{60}$ increases when charge is put in the T$_{1u}$ orbital. Thus when filling the LUMO the screening of the external field should become somewhat more efficient. Second, due to the electric field the molecular orbitals are deformed and thus the hopping matrix elements between neighboring molecules change. This effect depends sensitively on the orientation of the molecules but it typically leads to a slight decrease of the band width with applied field, making the Stark splitting even more important. Furthermore we have neglected the effect of electron-phonon coupling, which also tends to narrow the bands. This should be particularly important for the $H_u$-band. Finally, we have not considered correlation effects. It is known that, at integer filling, the alkali-doped Fullerenes are close to a Mott transition and that they are metallic because of orbital degeneracy. Due to the reduced coordination in two dimensions, a doped monolayer of C$_{60}$ should be even more strongly correlated, even if the orbitals are still degenerate. Lifting the degeneracy, e.g., by the Stark effect significantly increases correlations even further. It therefore seems inevitable that for an integer number of induced charges a C$_{60}$ monolayer will be a Mott insulator, even though it is not clear what effect the gate oxide might have on the Coulomb repulsion $U$ between two electrons on a C$_{60}$ molecule.

To summarize, it seems safe to conclude that the physics of field-effect devices based on C$_{60}$ as active material should be quite different from that of the alkali-doped fullerenes, at least at doping levels beyond two carriers per molecule.

Acknowledgments

The authors would like to thank O. Gunnarsson, T.M. Rice, B. Batlogg, and C. Helm for fruitful discussions. This work has been supported by the Swiss Nationalfonds.

APPENDIX A: RESPONSE FOR GENERAL ORIENTATION

To illustrate the use of the response coefficients given in table II we show, how to calculate the response for a multipole potential with $(l,m) = (30)$ for different orientations of the $z$-axis with respect to the C$_{60}$ molecule. This is the first non-trivial case, as the response for multipoles with $l \leq 2$ is isotropic. To start with, we need the basis functions $Y_{l,m}$ spanning the irreducible representation of the $I_h$, that were introduced in section III. For specific orientations, these can be found, e.g., in the Ref. 12, chapter 16, or Ref. 13, table 4.2. For arbitrary orientations, they have to be derived by explicitly finding the basis functions that span the irreducible representations of the icosahedral group. For the sake of the example, we consider the response for $z$ along the 5-fold and the 3-fold axis of the C$_{60}$ molecule. The corresponding basis functions are then both found in Ref. 12. Since we are interested in the response to an external multipole with $(l,m) = (30)$, we have to identify those basis functions that contain $Y_{30}$. They are shown in table VI. It turns out that for $z$ parallel to the 5-fold axis the $(30)$ potential corresponds to a pure $T_{2u}$ potential. Thus the

![FIG. 9: DOS (per molecule and for both spins) of the LUMO-band taking into account the level splitting for doping $q = 0, -1, -2$. The Fermi energy is indicated.](image)

![FIG. 10: As in figure but for the DOS of the HOMO-band with $q = 0, 1, 2, 3$.](image)
The 3-fold axis the situation is more complicated, as the potential is now a mixture of partner functions of $G_u$ and $T_{2u}$: As can be seen from table VI it mixes with the $Y_{3c3} = \sqrt{2} \text{Re}(Y_{33})$ component. By construction, the response matrix $\alpha$ in the subspace spanned by $\{Y_{30}, Y_{3c3}\}$ is diagonal, with diagonal elements $\alpha_{33}(H_u)$ and $\alpha_{33}(T_{2u})$, when written in the basis functions listed in table VI. However, to obtain the multipole response we have to use the basis $(Y_{30}, Y_{3c3})$, for which there are off-diagonal elements:

\[
\alpha = \frac{1}{9} \left[ 8 \alpha_{33}(H_u) + \alpha_{33}(T_{2u}) \right] \sqrt{\frac{2}{9}} \alpha_{33}(T_{2u}) - \alpha_{33}(H_u) + 8 \alpha_{33}(T_{2u}) \right].
\]

We thus find

\[
\Delta Q_{30} = \frac{1}{9} \left[ 8 \alpha_{33}(H_u) + \alpha_{33}(T_{2u}) \right] V_{30},
\]

\[
\Delta Q_{3c3} = \sqrt{\frac{2}{9}} \left[ \alpha_{33}(T_{2u}) - \alpha_{33}(H_u) \right] V_{30}.
\]

**APPENDIX B: COUPLING MATRICES**

In this section we discuss the calculation of the level splitting for arbitrary directions within perturbation theory using the coupling constants of table III. As discussed above, we restrict the analysis to $l = 1$ and $l = 2$ external potentials, which corresponds to $x = T_{1u}$ and $x = H_g$ potentials in the icosahedral symmetry $I_h$. In first order perturbation theory, the splitting of the levels in the degenerate subspace $E_{nx}$ is given by the eigenvalues of the matrix

\[
H_{k_1k_2}^{(1)}(nx) = \langle nxk_2|V_{\text{eff}}|nxk_1 \rangle.
\]

This matrix vanishes in the case of an odd potential and the splitting is given by the second order expression

\[
H_{k_1k_2}^{(2)}(nx) = \sum_{\langle n'x'k' \rangle} \sum_{k'} \frac{\langle nxk_2|V_{\text{eff}}|n'x'k' \rangle \langle n'x'k'|V_{\text{eff}}|nxk_1 \rangle}{E_{nx} - E_{n'x'}}.
\]

The matrix-elements in (11) and (12) are given in (11) and involve the icosahedral Clebsch-Gordan coefficients $C_{k_2k_1}^k(\lambda; x_2x_1; x)$. In order for the $k$-indices to be defined we consider the molecule oriented with the 5-fold axis parallel to the $z$-axis (see figure 1). This allows to label the states within a multiplet unambiguously with its $C_5$ index $k$. The ordered basis of a $T_{1u}$ subspace has $k$-indices $(0, 1, -1)$ whereas the ordered basis of an $H_u$ subspace is given by $(0, 1, -1, 2, -2)$. Note that in the case of applied $l = 1$ or $l = 2$ potential, the $k$ index corresponds to the $m$ index of the spherical harmonics. For a detailed discussion we refer to Ref. 12. We will present the coefficients $C_{k_2k_1}^k(\lambda; x_2x_1; x)$ as matrices with respect to the indices $k_1$ and $k_2$. In order to reduce the number of matrices, we will give the coupling matrices for $(lm) = (10), (20)$ potentials, which are rotated around the $y$-axis by an angle $\theta$. The resulting matrices are then given by

\[
C_{\lambda}(\lambda; x_2x_1; x) = \sum_k R_{\theta k}^l(\theta) C_{k_2k_1}^k(\lambda; x_2x_1; x),
\]

where $R_{\theta k}^l(\theta)$ is the rotation matrix of the spherical harmonics in a given $l$-subspace. Using the previous relations and equation (11), the coupling matrix for an even $l = 2$ potential is given by

\[
H^{(1)}(nx, \theta) = V_{20} \sum_{\lambda} t_{\lambda}(nx nx; H_g) C_{\lambda}^{(1)}(xx; H_g).
\]
Note that the multiplicity label \( \lambda \) is only relevant for the HOMO \( H_u \) because \( H_u \) occurs twice in the product \( H_u \otimes H_u = A_g \oplus T_{1g} \oplus T_{2g} \oplus 2G_g \oplus 2H_g \). The coupling matrix for the odd \( l = 1 \) potential is

\[
H^{(2)}(nx, \theta) = V_{10}^2 \sum_{(nx', x') = (nx) \atop x' \neq nx} \frac{t(nx nx'; T_{1u})^2}{E_{nx} - E_{nx'}} C^\theta(xx'; T_{1u})^T C^\theta(xx'; T_{1u}).
\]

(B5)

In the following we restrict the sum over subspaces \( \mathcal{E}_{nx'} \) closest in energy to \( \mathcal{E}_{nx} \) which is the \( T_{1u} \) subspace in the case of the LUMO and the \( H_g \) and \( G_g \) subspaces in the case of the the HOMO (see Fig 3). Below, the coupling matrices \( C^\theta(x_1 x_2; x) \) which are needed to calculate the splitting of the HOMO and LUMO are given. They are traceless \( \text{Tr} C^\theta = 0 \) and normalized such that \( \text{Tr} (C^\theta)^T C^\theta = 1 \). The coupling matrices which describe the splitting of the LUMO are

\[
C^\theta(T_{1u}T_{1g}; T_{1u}) = \frac{1}{2} \begin{pmatrix}
0 & -\sin \theta & -\sin \theta \\
-\sin \theta & -\sqrt{2} \cos \theta & 0 \\
-\sin \theta & 0 & \sqrt{2} \cos \theta \\
\end{pmatrix},
\]

(B6)

\[
C^\theta(T_{1u}T_{1u}; H_g) = \frac{1}{4} \begin{pmatrix}
-4 \sqrt{\frac{2}{3}} + 2 \sqrt{6} \sin^2 \theta & \sqrt{6} \sin 2\theta & -\sqrt{3} \sin 2\theta \\
\sqrt{3} \sin 2\theta & 2 \sqrt{\frac{2}{3}} - \sqrt{6} \sin^2 \theta & \sqrt{6} \sin^2 \theta \\
-\sqrt{3} \sin 2\theta & \sqrt{6} \sin^2 \theta & 2 \sqrt{\frac{2}{3}} - \sqrt{6} \sin^2 \theta \\
\end{pmatrix}.
\]

(B7)

The eigenvalues of these two matrices are independent of \( \theta \) and given by \((0, -\frac{1}{2}, \frac{1}{2})\) and \((-\frac{3}{4}, \frac{1}{4}, \frac{1}{4})\) which implies that the splitting is independent of the orientation of the molecule with respect to the direction of the applied \( l = 1 \) and \( l = 2 \) potentials. The coupling of the HOMO \( (H_u) \) to the lower lying \( H_g \) and \( G_g \) levels is given by

\[
C^\theta(H_u H_g; T_{1u}) = \frac{1}{2 \sqrt{3}} \begin{pmatrix}
0 & \sqrt{3} \sin \theta & -\sqrt{3} \sin \theta & 0 & 0 \\
\sqrt{3} \sin \theta & -\sqrt{2} \cos \theta & 0 & \sqrt{2} \sin \theta & 0 \\
-\sqrt{3} \sin \theta & 0 & \sqrt{2} \cos \theta & 0 & -\sqrt{2} \sin \theta \\
0 & \sqrt{2} \sin \theta & 0 & -2 \sqrt{2} \cos \theta & 0 \\
0 & 0 & -\sqrt{2} \sin \theta & 0 & 2 \sqrt{2} \cos \theta \\
\end{pmatrix},
\]

(B8)

\[
C^\theta(H_u G_g; T_{1u}) = \frac{1}{2 \sqrt{3}} \begin{pmatrix}
\sqrt{3} \sin \theta & 2 \sqrt{2} \cos \theta & 0 & -\sqrt{3} \sin \theta & 0 \\
-\sqrt{3} \sin \theta & 0 & -2 \sqrt{2} \cos \theta & 0 & \sqrt{3} \sin \theta \\
0 & -\sqrt{2} \sin \theta & 0 & -\sqrt{2} \cos \theta & -\sqrt{3} \sin \theta \\
0 & 0 & \sqrt{2} \sin \theta & -\sqrt{3} \sin \theta & \sqrt{2} \cos \theta \\
\end{pmatrix}.
\]

(B9)

The coupling of the HOMO among themselves is given by

\[
C^\theta(1; H_u H_u; H_g) = \frac{1}{4 \sqrt{3}} \begin{pmatrix}
-8 + 12 \sin^2 \theta & \sqrt{2} \sin 2\theta & \sqrt{2} \sin 2\theta & \sqrt{2} \sin^2 \theta & \sqrt{2} \sin^2 \theta \\
\sqrt{2} \sin 2\theta & 2 - 3 \sin^2 \theta & -3 \sin^2 \theta & -3 \sin 2\theta & 3 \sin^2 \theta \\
\sqrt{2} \sin 2\theta & -3 \sin^2 \theta & 2 - 3 \sin^2 \theta & 3 \sin^2 \theta & -3 \sin 2\theta \\
\sqrt{2} \sin^2 \theta & -3 \sin 2\theta & 3 \sin^2 \theta & 2 - 3 \sin^2 \theta & 3 \sin 2\theta \\
\sqrt{2} \sin^2 \theta & 3 \sin^2 \theta & -3 \sin 2\theta & 3 \sin 2\theta & 2 - 3 \sin^2 \theta \\
\end{pmatrix},
\]

(B10)

\[
C^\theta(2; H_u H_u; H_g) = \frac{1}{4} \begin{pmatrix}
0 & \sqrt{2} \sin 2\theta & \sqrt{2} \sin 2\theta & -\sqrt{2} \sin^2 \theta & -\sqrt{2} \sin^2 \theta \\
\sqrt{2} \sin 2\theta & 2 - 3 \sin^2 \theta & \sin^2 \theta & \sin 2\theta & \sin^2 \theta \\
\sqrt{2} \sin 2\theta & \sin^2 \theta & 2 - 3 \sin^2 \theta & \sin^2 \theta & \sin 2\theta \\
-\sqrt{2} \sin^2 \theta & \sin 2\theta & \sin^2 \theta & -2 + 3 \sin^2 \theta & \sin 2\theta \\
-\sqrt{2} \sin^2 \theta & \sin^2 \theta & \sin 2\theta & \sin 2\theta & -2 + 3 \sin^2 \theta \\
\end{pmatrix}.
\]

(B11)
In equation (B3), the product $c^{th}(xx'; T_{1u})^T c^{th}(xx'; T_{1u})$ enters. For the matrices given in (B6), (B8) and (B9) these products can be expressed in terms of the $l = 2$ coupling matrices (B7), (B10) and (B11):

$$c^{th}(T_{1u}T_{1g}; T_{1u})^T c^{th}(T_{1u}T_{1g}; T_{1u}) = \frac{1}{3} + \frac{1}{\sqrt{6}} c^{th}(T_{1u}T_{1u}; H_g),$$  \hspace{1cm} (B12)

$$c^{th}(H_u H_g; T_{1u})^T c^{th}(H_u H_g; T_{1u}) = \frac{1}{5} + \frac{\sqrt{5}}{10} c^{th}(1; H_u H_u; H_g) - \frac{3}{10} c^{th}(2; H_u H_u; H_g),$$  \hspace{1cm} (B13)

$$c^{th}(H_u G_g; T_{1u})^T c^{th}(H_u G_g; T_{1u}) = \frac{1}{5} + \frac{\sqrt{5}}{10} c^{th}(1; H_u H_u; H_g) + \frac{3}{10} c^{th}(2; H_u H_u; H_g).$$  \hspace{1cm} (B14)

Using these relations, the total coupling matrix (neglecting the constant terms in the previous relations) due to the applied $l = 1$ and $l = 2$ potential, is given by

$$H'(T_{1u}, \theta) = \left(V_{10}^2 c_1 + V_{20} c_2\right) c^{th}(T_{1u}T_{1u}; H_g),$$  \hspace{1cm} (B15)

$$H'(H_u, \theta) = V_{10}^2 \left[\cos \delta_1 c^{th}(1; H_u H_u; H_g) + \sin \delta_1 c^{th}(2; H_u H_u; H_g)\right] +$$

$$V_{20} \left[\cos \delta_2 c^{th}(1; H_u H_u; H_g) + \sin \delta_2 c^{th}(2; H_u H_u; H_g)\right],$$  \hspace{1cm} (B16)

where $c_1 = \frac{1}{\sqrt{6}} \left(\frac{(H_u H_u T_{1u})^2}{E_{H_u - E_{T_{1u}}} + (H_u H_u T_{1u})^2}\right)$ and $c_2 = t(T_{1u}T_{1u}; H_g)$. Similarly we have $d_1 \cos \delta_1 = \sqrt{10} \left[\frac{(H_u H_u T_{1u})^2}{E_{H_u - E_{T_{1u}}} + (H_u H_u T_{1u})^2}\right]$, $d_1 \sin \delta_1 = \frac{3}{10} \left[\frac{(H_u H_u T_{1u})^2}{E_{H_u - E_{T_{1u}}} + (H_u H_u T_{1u})^2}\right]$ and $d_2 \cos \delta_2 = t_1 (H_u H_u; H_g)$, $d_2 \sin \delta_2 = t_2 (H_u H_u; H_g)$. Equation (B15) implies that the contributions of the $l = 1$ and $l = 2$ to the splitting of the LUMO add up trivially. Using the values in table (I) and the energies of figure 3 yields the values $\delta_1 = 0.064$ and $\delta_2 = 0.037$, which are almost equal when compared to $\pi$. This can be understood by the following remarks: $\delta_1 = 0$ in the case of $t(H_u H_g; T_{1u}) = t(H_u G_g; T_{1u})$ and $E_{H_g} = E_{G_g}$. Furthermore, it can be shown that $\delta_2 = \arctan(1/\sqrt{25}) \approx 0.090$ assuming that the angular dependence of the HOMO is given by $l = 5$ spherical harmonics. Taking an average value of $\delta = 0.050$ yields the approximate relation

$$H'(H_u, \theta) \approx \left(V_{10}^2 d_1 + V_{20} d_2\right) \left[\cos \delta C^{th}(1; H_u H_u; H_g) + \sin \delta C^{th}(2; H_u H_u; H_g)\right],$$  \hspace{1cm} (B18)

which shows that, to a good approximation, the contributions of the $l = 1$ and $l = 2$ potential to the splitting of the HOMO add up trivially.

**APPENDIX C: CALCULATION OF THE MATRIX $\beta$**

In this section it is shown how to calculate the matrix $\beta$ appearing in equation (16). The second term on the right side of this equation describes the coefficients of the term $\sum_{\text{neighbors}} V(r - R_i)$ which enters the screened potential $V^{scr}$ and which describes the potential induced by all neighboring sites. Using the definition (1), we can rewrite this expression as

$$\sum_{\text{neighbors}} V(r - R_i) = \sum_{l_m} Q_{lm} \sum_{\text{neighbors}} I_{lm}(r - R_i) = \sum_{l_m} Q_{lm} \left(-1\right)^m I_{m-l}(r - R_i).$$  \hspace{1cm} (C1)

The function $I_{lm}(r_1 - r_2)$ can be decomposed using the translation formula (for $r_1 < r_2$)

$$I_{LM}(r_1 - r_2) = \sum_{l_1 m_1, l_2 m_2} (-1)^{l_2} \sqrt{2(L + 1)! / (2l_1)l_1} \sum_{m_1 m_2} C_{l_1 m_1 l_2 m_2}^{LM} r_{12}(r_1) I_{l_2 m_2}(r_2),$$  \hspace{1cm} (C2)

where $C_{l_1 m_1 l_2 m_2}^{LM}$ denote the Clebsch-Gordan coefficients. This formula can be found in different forms in the literature, see for example Ref. 14. 17. Substituting (C2) in the sum (C1) with $r_1 = r$ and $r_2 = R_i$ yields

$$\sum_{\text{neighbors}} V(r - R_i) = \sum_{l_1 m_1, l_2 m_2} \beta_{l_1 m_1 l_2 m_2} Q_{l_2 m_2} R_{l_1 m_1}(r),$$  \hspace{1cm} (C3)
where the matrix $\beta$ is given by

$$
\beta_{l_1 m_1 l_2 m_2} = (-1)^{m_2+l_2} \sqrt{\frac{(2(l_1+l_2))!}{(2l_1)! (2l_2)!}} C_{l_1 m_1 l_2 m_2}^{l_1+l_2 m_1-m_2 \mathbf{R}_i} \sum_{\mathbf{R}_j \neq 0} I_{l_1l_2 m_1-m_2} (\mathbf{R}_i)
$$

(C4)

$$
= (-1)^{m_2+l_2} \frac{(l_1+l_2+m_1-m_2)! (l_1+l_2-m_1+m_2)!}{(l_1+m_1)! (l_1-m_1)! (l_2+m_2)! (l_2-m_2)!} \sum_{\mathbf{R}_j \neq 0} I_{l_1l_2 m_1-m_2} (\mathbf{R}_j)
$$

In the last equality in (C4) the explicit form of the Clebsch-Gordan coefficients was used. One verifies, that the matrix $\beta$ is complex conjugate under the exchange of all indices. The remaining sums over the lattice sites $\mathbf{R}_j$ in (C4) are easily performed by computer.