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1997 J. Phys.: Condens. Matter 9 157

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Coulomb interaction in self-consistent field calculations on molecules in molecular crystals

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Received 24 May 1996, in final form 20 August 1996

Abstract. A method of direct calculation of Madelung sums in molecular crystals is proposed. It is based on preliminary evaluation of Coulomb interaction of two contrarily charged elements of a crystal cell translated over the whole crystal. As a result some Madelung parameters similar to Coulomb integrals enter the molecular crystal Hartree–Fock equations whose dimensionality remains the same as for the isolated molecule. As an illustration of this approach the alteration of the hyperpolarizability tensors of urea and triaminotrinitrobenzene (TATB) molecules are calculated when these molecules enter a crystal. A possible explanation of the second-harmonic generation ability by TATB is given.

1. Introduction

In recent years, much attention has been paid to the calculation of non-linear electrical properties of molecular crystals (see, e.g., [1] and other papers in that issue). The most interesting problem is the change in the properties of a separate molecule when it is placed into a crystal. This change is determined by the changed electron distribution caused by similar molecules in a crystal with the same altered electron density. The account of polarization of molecular electron clouds is necessary to describe this intermolecular influence. This is an additional problem compared with calculation of the packing energy which is often done by means of the atom–atom potentials usually taking the Buckingham form

$$V(r) = A \exp(-ar) - B/r^6. \quad (1)$$

This scheme with the constants A , B and a , which are easily adjusted for each type of atom of a chosen molecular crystal class, gives satisfactory results for the sublimation energy, molecular positions and crystal cell parameters (see, e.g., [2]). However, the polarization problem is outside the framework of this approach. Moreover, this scheme has a conceptual drawback, considering the intermolecular (1) and intramolecular electronic Coulomb interactions in quite different manners.

There are various methods accounting for molecular polarization and interaction. In the cluster method [3] the Hartree–Fock approximation is applied to a ‘supermolecule’ consisting of all molecules which enter the same crystalline cell and interact through the Coulomb term of the Fock operator. This procedure does not reflect the true crystal symmetry and therefore the calculated first hyperpolarizability tensor contains incorrect non-zero components [3]. The more rigorous reaction field method [4] can hardly be used for calculation of the equilibrium positions of molecules in the unit cell and other parameters,

except for susceptibilities. An interesting way to account for the real crystal symmetry is used in [5] where the Coulomb forces are included in the Fock operator which originates from atoms of the adjacent cells confined by the hydrogen bonds to the molecules from the cell considered. The charges on the adjacent atoms repeat the corresponding charges obtained from the Hartree–Fock calculation of the cell under consideration. An additional self-consistency procedure over these charges guarantees the desired symmetry. Another way to account for the crystal symmetry has already been proposed in [6]. An alternative possibility for reproducing the correct molecular properties in a crystal is to calculate the number of higher and inhomogeneous (quadrupole, octupole, etc) polarizabilities in the spirit of [7] and then to use them to determine the reaction field.

Here we shall follow a direct way which allows one to find the ground state of molecules in a crystal, as well as hyperpolarizabilities similarly to the free molecule, e.g. by the Hartree–Fock method. The potential created by all molecules of the crystal with an identical electron distribution enters only the Coulomb term in the Fock operator since molecular wavefunctions are assumed not to overlap as in [3, 5, 8]. However, in our case, each element of charge is repeated periodically and serves as the origin of the Madelung potential. Certainly, this potential should be recalculated in every cycle of the Hartree–Fock self-consistency process together with the electron distribution. This procedure seems to be very cumbersome. Nevertheless, as is shown below, the Madelung formula applied to the volume case [9], which can be used for arbitrary crystals [10], allows one to simplify this scheme significantly. The proposed procedure generalizes the calculation method of molecular ion polarization by the lattice of fixed point charges [11] to the translationally invariant set of variable charges. The relation of this scheme to the previous papers on the Madelung constant calculation has been discussed in [9–11]. In addition we mention a general treatment of the problem by Williams [12] and the recent work of Hummer [13] on the numerical accuracy of the Ewald method.

The main present idea is that the Madelung interaction of an arbitrary pair of cell ‘elements’ may be calculated beforehand similarly to the Madelung constants or to integrals between basis orbitals. As a result the self-consistency procedure for the molecule in a crystal is not more complicated than that for the free molecule. Only Coulomb interaction integrals obtain increments from the ‘pair Madelung constants’. Hence infinite summation in each Hartree–Fock iteration is avoided.

In section 3 the proposed scheme is illustrated by calculation of the first hyperpolarizability tensor increments for the urea and triaminotrinitrobenzene (TATB) crystals.

2. The calculational method

As was shown in [10], the potential at a point $r(x, y, z)$ of the crystal cell created by unit charges placed at a point $R(X, Y, Z)$ of the same cell and at all points, obtained by its translation, and also by compensating charges of -1 at the origin of each cell can be presented in the form

$$V(r, R) = S(\rho_1, x, X) + S(\rho_2, y, Y) + S(\rho_3, z, Z). \quad (2)$$

Here coordinates are measured in units of the period a along, for example, the z axis and

$$S(\rho, z, Z) = F(\rho, z) - F(\rho, z - Z) \quad (3)$$

$$F(\rho, z) = 4 \sum_{l=1}^{\infty} K_0(2\pi l\rho) \cos(2\pi lz) \quad \rho \neq 0 \quad (4)$$

$$F(O, z) = \frac{1}{z(1-z)} + 2z \sum_{k=1}^{\infty} \frac{1}{k(k^2 - z^2)} \quad (4')$$

$$\rho_1 = \sqrt{y^2 + z^2} \quad \rho_2 = \sqrt{(x-X)^2 + z^2} \quad \rho_3 = \sqrt{(x-X)^2 + (y-Y)^2}. \quad (5)$$

The convergence of the series (4) of the McDonald functions K_0 is rather rapid since, in the real case, ρ is far from zero.

These equations may be used for molecular crystals as well. When a molecular wavefunction is built of linear combinations of atomic orbitals, the natural discretization of molecular charge appears. Namely,

$$P_{ss} = 2 \sum_i^{occ} c_{is}^2 \quad (6)$$

is the charge ascribed to the s th atomic orbital according to the Mulliken [14] population analysis (c_{is} are the orbital expansion coefficients). This charge creates the Coulombic potential of type $1/|r - r_A|$ where r_A is the centre of the s th orbital. As a result in the first approximation the term

$$D_{tt} = \sum_{A(\neq B)} \frac{Q_A}{R_{AB}} \quad (7)$$

appears in the diagonal matrix element F_{tt} of the Fock operator where R_{AB} is the distance between the nuclei A and B of different molecules (the orbital t belongs to B), $Q_A = P_A - Z_A$, Z_A is the nuclear charge and P_A is the 'gross population' [14] of the atom A, given by

$$P_A = \sum_{s \in A} P_{ss}. \quad (8)$$

Thus each diagonal matrix element F_{tt} of the 'atom' B obtains an increment D_{tt} (7) when a molecule is placed into a crystal. As a consequence of the orbital orthogonality,

$$\sum_A P_A = \sum_{s=1}^m P_{ss} = N \quad (9)$$

N is the total electron number, and the 'atom' is a set of basis orbitals centred at some nucleus. Therefore

$$\sum_A Q_A = N - \sum_A Z_A = 0 \quad (10)$$

is the total molecular charge which we have assumed to be zero. In fact, sum (7) approximates the expression

$$\sum_{s=1}^m P_{ss}(ts|ts) - \sum_A Z_A U_{A,tt} \quad (11)$$

where the standard notation for electron repulsion integrals is used, and $U_{A,tt} = \int \chi_t^2(r) dV / |r - R_A|$ is the nuclear attraction integral. Equation (7) is valid at large internuclear distances, i.e. just in the region essential for calculation of crystal sums. If necessary, some nearest-neighbour terms in equation (7) may be replaced by expressions of type (11).

For clarity the case when each ‘atom’ consists of a single orbital (e.g. in the π -electron systems) will be considered in more detail. In this case the additional contribution to the diagonal element (9) is reduced to

$$D_{tt} = \sum_l \sum_{s=1}^m \frac{Q_s}{R_{ts(l)}}. \quad (12)$$

$R_{ts(l)}$ is the distance between the centre of the t th orbital of the zero cell and the centre of the s th orbital in a cell with the origin at l , and Q_s is the residual π charge. The first summation \sum_l in (12) is taken over all crystal cells and the second over all basis orbitals of the molecule considered. We cannot interchange the summations directly. However, as a consequence of (10) ($\sum_{s=1}^m Q_s = 0$) we can subtract from (12) the zero sum $\sum_{s=1}^m Q_s \sum_l 1/|l|$ and present D_{tt} in the form

$$D_{tt} = \sum_{s=1}^m Q_s \sum_l \left(\frac{1}{R_{ts(l)}} - \frac{1}{|l|} \right). \quad (13)$$

The internal sum is just the Madelung potential as defined in equation (2). It depends on the position of the t th and s th points in the zero crystal cell:

$$D_{tt} = \sum_{s=1}^m Q_s V(t, s). \quad (14)$$

Now it is evident that the same transformation may be used when the crystal is built up of identical molecular ions whose charge $Q = \sum Q_s \neq 0$ is compensated by the point charges $-Q$ situated at the origin of each cell.

It should be noted that $V(t, s) \neq V(s, t)$. However, $V(t, s) - V(t, t)$ according to the definition (2) describes the Madelung potential at the point t when the point charge -1 is placed at it whereas the charge $+1$ is situated at s . Obviously $V(s, t) - V(s, s)$ gives the same potential since it does not depend on simultaneous change in signs of both charges. Therefore

$$V_{ts} \equiv V(t, s) - V(t, t) = V(s, t) - V(s, s) = V_{st}. \quad (15)$$

The substitution of (15) into (14) leads to

$$D_{tt} = \sum_{s=1}^m Q_s (V_{ts} + V(t, t)) = \sum_{s=1}^m Q_s V_{ts} + V(t, t) \sum_{s=1}^m Q_s = \sum_{s=1}^m Q_s V_{ts}. \quad (16)$$

Including the term D_{tt} in the diagonal element of the Fockian, we must bear in mind that the latter already contains the interaction between orbitals t and s in its Coulomb part if these both belong to the same molecule. Therefore the final result is

$$U_{ts} = V_{ts} - \begin{cases} 1/R_{ts} \\ 0. \end{cases} \quad (17)$$

The first formula should be used if both centres belong to the same molecule while the second formula has to be applied if t and s are in different molecules (in crystals which contain more than one molecule in the unit cell).

Since the Coulomb term in the Fockian usually looks like $\sum_{s=1}^m \gamma_{ts} Q_s$, the only difference between the calculation of the isolated molecule and the same molecule in a crystal is that the Coulomb repulsion integrals γ_{ts} in the second case should be replaced by $\gamma_{ts} + U_{ts}$. Applying this simple final prescription also to the coupled Hartree–Fock perturbation theory, to the random-phase approximation, etc, we can suitably modify the corresponding computer programs for an isolated molecule [15, 16] and calculate the change in hyperpolarizabilities, electron transitions, etc, for molecules in crystals.

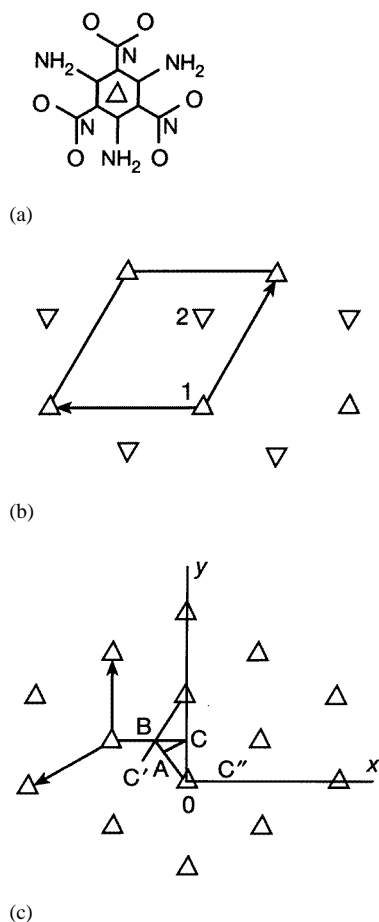


Figure 1. (a) Notation of TATB for (a) and (b). (b) The centrosymmetric hexagonal plane layer with two molecules in a cell. The lattice vectors are shown. (c) The non-centrosymmetric trigonal plane layer. x , y are simultaneously coordinates of the projection of the end of the third lattice vector (for the lattice $P1$) or the coordinate origin of the intermediate layer (for the lattice $P\bar{1}$). c , c' , c'' show three possible different equivalent positions of the origin of the intermediate layer in $P\bar{1}$.

3. Some illustrative model calculations

3.1. Urea crystal of symmetry $P\bar{4}2_1m$

The simplest example which we shall consider in the π -electron approximation is the urea crystal of symmetry $P\bar{4}2_1m$ containing two molecules in a cell with parameters $a = 5.67 \text{ \AA}$ and $c = 4.73 \text{ \AA}$ [17]. Here the matrix \mathbf{U} consists of two identical diagonal blocks which describe interactions only with all other cells while the non-diagonal block includes the action of atoms from the same cell.

From equation (15) it is clear that always $U_{ss} = 0$. The matrix \mathbf{U} is determined only by the cell parameters and positions of the corresponding points (s, t) in a cell. It is independent both of the cell content and of the method of calculation of the electronic state of a molecule.

Therefore U_{st} may be calculated beforehand for many cases as well as the usual Madelung constants.

With the \mathbf{U} -values calculated, the atomic net charges obtained are 0.223 on N, -0.738 on O, and 0.292 on C and they change compared with the values for the free molecule which are 0.180, -0.651 and 0.291, respectively. As a result of the charge transfer from N to O the dipole moment increases from 5.1 to 5.9 D. The Madelung energy per cell is -1.303 eV, which corresponds to the general energy lowering of 1.128 eV for the pair of molecules. It should be emphasized that all these values have been obtained accounting only for Coulomb forces which themselves cannot guarantee the core repulsion arising from the overlap of wavefunctions. However, as is known, new solutions may appear at the instability threshold of the Hartree–Fock equations [18]. This peculiarity of the Hartree–Fock approach is directly connected to the problem considered. If two molecules in a unit cell are located too close (this can be modelled by a decrease in the lattice parameter a), then collapse occurs at some value of the parameter a before it reaches the sum of the geometrical sizes of molecules in a cell in spite of ignoring the wavefunction overlap and the core repulsion. Namely, the crystal turns into the ionic form; one molecule transfers into a dication and the other into a dianion.

Thus, a reasonable qualitative picture is obtained without any adjustment parameters. The π -electron Hamiltonian used has been fitted to reproduce the non-linear optical properties of benzene, styrene and stilbene derivatives not including urea [15, 16]. Therefore the description of the non-linear optical properties of this crystal is of some interest. As a consequence of the crystal symmetry, most β_{ijk} components in the crystal, except for β_{xyz} , are zero. Nevertheless, since each molecule is characterized by its own wavefunction as a result of neglect of the overlap, we can calculate the properties of the individual molecule in a crystal in quite a standard manner. In the approximation used, there are only two non-zero components of the first hyperpolarizability tensor $\beta_{yyy} = -60.0$ au and $\beta_{xxy} = 108.8$ au, where the y axis coincides with the molecular symmetry axis, and the x axis lies in the molecular plane. The calculation for the free molecule gives $\beta_{yyy} = -46.0$ au and $\beta_{xxy} = 83.5$ au. These results are in a reasonable agreement with the best non-empirical calculation for urea [5] where for the free molecule it has been found that $\beta_{yyy} = -44.1$ au and $\beta_{xxy} = 23.1$ au and, for the molecule in a crystal, $\beta_{yyy} = -74.1$ au and $\beta_{xxy} = 31.5$ au. For comparison a model crystal of the same molecules with parallel orientation has also been considered. In this case, $\beta_{yyy} = -71.6$ au and $\beta_{xxy} = 121.3$ au.

3.2. The triaminotrinitrobenzene crystal

Our second illustration is the TATB crystal [2]. The interest in this system has arisen after demonstration of that this centrosymmetric crystal [19] is able to generate the second harmonic [20]. In [2] it was supposed that the second-harmonic generation is due to the presence of domains with identical orientations of molecules in adjacent layers since an approximately equal packing energy for parallel and antiparallel orientations in the neighbouring layers has been found. The present approach leads to a similar conclusion. Additionally it will be established that hyperpolarizability of the TATB molecule in the crystal increases by more than three times compared with the free molecule for both orientation types. This allows us to give a more detailed explanation of why the net β_{ijk} in the crystal is non-zero.

Two types of plane elementary cell have been considered in [20]: hexagonal centrosymmetric and trigonal without a centre of symmetry (figure 1). For the experimental lattice parameters [19] $a = 9.02$ Å and $\beta = 120^\circ$, the π -electron calculation with the

Hamiltonian [15] reveals that the hexagonal layer is unstable as a consequence of the large positive Madelung energy, 1.22 eV, while the trigonal layer manifests a small Coulomb binding energy of 0.05 eV which corresponds to the assumptions made [20]. (The hydrogen bonds are not considered explicitly.) Then the relative positions of adjacent, identically oriented layers have been optimized for the interlayer distance $h = 3.138 \text{ \AA}$. The energy minimum occurs for a relative shift of $y = a/2$ which corresponds to the remaining cell parameters $c = 5.495 \text{ \AA}$, $\alpha = 114.23^\circ$ and $\gamma = 34.83^\circ$ of the $P1$ -type lattice. As is clear from figure 2, where the potential surface above the triangle OBC (figure 1) is presented, the above cell parameters ensure an absolute minimum with respect to sliding of the layers. The calculated Madelung energy is -0.791 eV and the packing energy is 0.515 eV . This structure is characterized by a significant increase in the hyperpolarizability tensor components of the free molecule: $\beta_{xxy} = -\beta_{yyy} = 1403 \text{ au}$ which become $\beta_{xxy} = 4179 \text{ au}$ and $\beta_{yyy} = -6277 \text{ au}$.

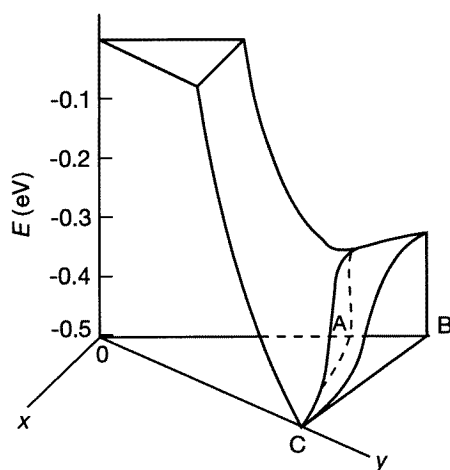


Figure 2. The independent section of the potential surface for the $P1$ lattice above the triangle OBC (see figure 1). The lattice energy is shown as a function of coordinates of the third lattice vector projection onto the layer plane. The whole potential surface is composed of six similar parts.

In the above $P1$ lattice, each two next-neighbour layers are not shifted relatively. Therefore we can use the same system with the cell parameters $\alpha = \gamma = 90^\circ$, $\beta = 120^\circ$, $a = 9.02 \text{ \AA}$, $c = 2h = 6.277 \text{ \AA}$ and two molecules per cell as the starting point for the centrosymmetric $P\bar{1}$ lattice if the second molecule is rotated by 60° (180°) around the z axis. A small displacement (0.29 \AA) of the second molecule along the y axis is necessary to obtain the energy minimum in this case since NO_2 groups are repulsed slightly more strongly than are NH_2 groups. As a result the packing energy per molecule becomes 0.537 eV . When moving from the middle ($y = 4.51 \text{ \AA}$) to the minimum ($y = 4.80 \text{ \AA}$), the hyperpolarizability decreases from $\beta_{yyy} = -6067 \text{ au}$ and $\beta_{xxy} = 4083 \text{ au}$ to $\beta_{yyy} = -5567 \text{ au}$ and $\beta_{xxy} = 4031 \text{ au}$.

The non-central position of the minimum on the lattice vector line gives an additional argument for the generation ability of the TATB crystal. There are three equivalent positions of the minimum on each of the three hexagonal-type lattice vectors mutually rotated by

120° in the molecular plane. The adjacent layer may take any of these. The crystal would be exactly centrosymmetric if every adjacent layer were moved in the same direction (of the three possible) or if it were displaced exactly by half the lattice vector. Otherwise the TATB symmetry axis cannot be directed simultaneously to the molecular centres of the nearest-neighbour and the next-neighbour layers, which leads to a small rotational perturbation of each TATB molecule. Thus, each irregular alternation of layers, in the above sense, will perturb the centrosymmetric orientation of molecules in the crystal cell. The deviation, e.g. by only 1° from 60°, induces a non-zero β of a cell with the norm $\|\beta\| = \sqrt{\beta_{ijk}\beta_{ijk}} = 321$ au (the octupolar norm [21] is 318.9 au) which is three times greater than the total above-calculated value of β in the urea crystal. The energy rise accompanying this rotation is less than 0.001 eV which is much smaller than that required (0.022 eV) for parallel arrangement of layers and may be cancelled by the above-mentioned perturbation.

4. Conclusion

A method of direct inclusion of the intermolecular Coulomb interactions between molecular electronic clouds into crystal Hartree–Fock equations is proposed. The latter retain the same form and dimension as for the isolated molecule and guarantee the correct crystal symmetry. The method admits a proper description of the mutual influence of molecules in a crystal on their electronic properties which depend only on the model used for calculation of the isolated molecule. The simplified examples of urea and TATB crystals considered demonstrate that this scheme is able to estimate their first hyperpolarizabilities.

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