

Nonempirical molecular orbital calculations for hydrogen bonded molecular solids: Molecular dipole and quadrupole moments for solid HF and HCl

S. G. Anderson and D. P. Santry

Citation: *The Journal of Chemical Physics* **74**, 5780 (1981); doi: 10.1063/1.440890

View online: <http://dx.doi.org/10.1063/1.440890>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/74/10?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Dipole and quadrupole moment functions of the hydrogen halides HF, HCl, HBr, and HI: A Hirshfeld interpretation](#)

J. Chem. Phys. **128**, 114320 (2008); 10.1063/1.2897445

[Hydrogen bonding: The structure of HF–HCl](#)

J. Chem. Phys. **67**, 5162 (1977); 10.1063/1.434691

[A nonempirical molecular orbital study on the acidity of the carbon–hydrogen bond](#)

J. Chem. Phys. **67**, 517 (1977); 10.1063/1.434907

[Dipole Moments, Nuclear Quadrupole Coupling, and the Bonding Orbitals in Group V—Trihalides](#)

J. Chem. Phys. **22**, 86 (1954); 10.1063/1.1739863

[Ionic Character and the Dipole Moment of Chemical Bonds. Calculations of the Dipole Moment of HCl](#)

J. Chem. Phys. **17**, 1022 (1949); 10.1063/1.1747107



Nonempirical molecular orbital calculations for hydrogen bonded molecular solids: Molecular dipole and quadrupole moments for solid HF and HCl

S. G. Anderson and D. P. Santry

Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1

(Received 8 December 1980; accepted 5 February 1981)

Ab initio SCF calculations, using the SCF perturbative method proposed by O'Shea and Santry, with a 3-21G basis set are reported by solid HF and HCl. It is found that the convergence of the perturbative series is slightly better than that for the corresponding CNDO theory. The calculated changes in the molecular dipole and quadrupole moments, induced by the crystal interactions, are found to be about 20% of their free molecule values.

INTRODUCTION

Unit cell electron density maps¹ obtained for molecular crystals by means of x-ray and neutron diffraction provide a basis for a detailed critical evaluation of the quality of theoretical electron densities derived from approximate wave functions. Before a comparison can be made between the theoretical and experimental electron density maps it is necessary, however, to correct the free molecule electron densities for the polarization effects of the crystal lattice. To do this consistently, it is, in effect, necessary to undertake a calculation for the electron distribution for the entire three dimensional lattice of interacting molecules.

A method for carrying through such a calculation has been proposed by O'Shea and Santry^{2,3} using SCF perturbation theory. One distinct advantage this approach has over the conventional Bloch orbital approach is that it leads to a direct calculation of the crystal density matrix, thereby circumventing the computational effort associated with the transformation properties of wave-vector dependent crystal orbitals. Crystal symmetry still has an important role in the theory, but instead of being used to construct symmetry adapted orbitals, it is used directly to equate crystallographically equivalent elements of the density matrix. Once this density matrix has been calculated it can be used to calculate the properties of the lattice molecules and to plot the unit cell electron distribution.

The above theory has been programmed for crystals with space-group symmetries up to and including orthorhombic. Although this excludes the high symmetry space groups, in practice it is sufficient for the study of most molecular crystals of chemical interest. Provision has been made to calculate several molecular properties but the unit cell electron density plotting algorithm remains to be completed.

In the present paper we report exploratory calculations for the molecular dipole and quadrupole moments of HF and HCl in their solids. As the hydrogen bonding in these materials is exceptionally strong, they provide a good test of the convergence properties of the theory discussed here. It is reasoned that if the method works well for these systems, it can be profitably applied to other, more weakly bonded, crystals.

THEORY

The objective here is the solution of the Roothaan⁴ SCF matrix equation

$$FC = SCE, \quad (1)$$

where F , C , S , and E are, respectively, the Fock, orbital coefficient, overlap, and orbital energy matrices, for a three dimensional crystal by means of SCF perturbation theory. As the means by which this can be accomplished have been discussed in detail elsewhere,² only a broad outline is appropriate here. The method proceeds by first partitioning all matrices in the above equation, with the exception of C , into intra- and intermolecular submatrices by a molecule by molecule ordering of the atomic orbital basis set. The crystal is treated at the zeroth order as a lattice of properly oriented but noninteracting molecules, and the neglected interactions are subsequently included as an SCF perturbation. By this means the problem of solving the single SCF matrix equation for the entire crystal is transformed to that of solving a large number of coupled SCF perturbation submatrix equations of dimension equal to that of an isolated lattice molecule. These equations cannot be conveniently solved for the crystal orbitals because of the high level of degeneracy present in the zero order states. Consequently, they are solved for the density submatrices instead, and the full crystal density matrix subsequently built up from them. It is sufficient for this purpose to calculate only those density submatrices which are crystallographically independent, i.e., those which cannot be generated one from the other by the application of an element from the crystal's space group.

The above procedure entails the calculation of an intramolecular density submatrix for each unique molecule in the unit cell, together with all of the independent intermolecular density submatrices involving these molecules and the molecules in the surrounding lattice. In practice it is usually sufficient to include only molecules up to the next nearest neighbors. The level of computational effort required for these calculations can be appreciably reduced, at the cost of an order of magnitude increase in program complexity, by taking full advantage of the point group symmetry of the crystal's lattice in addition to its simple translational symmetry.

For example, in the calculations to be reported here, the translational symmetry reduced the number of coupled submatrix equations to be solved in order to complete the crystal density matrix from an almost infinite number to 44. The point group symmetry further reduced this number to four, with a corresponding reduction in the number of integrals to be calculated.

The organization of the calculation begins with the selection of a reference unit cell and the identification of the independent molecules within it. Each unique molecule is chosen in turn as the origin and the surrounding lattice scanned within a sphere of prescribed radius, here chosen to include third nearest neighbors, for intermolecular contacts. The intermolecular density submatrices for all pairs of molecules found in this scan are, together with the intramolecular matrices, calculated and included in the formation of the Fock submatrices: all other intermolecular submatrices, involving the same reference molecules, have longer intermolecular distances and are therefore assumed to be negligible.

The definition of the intermolecular perturbation and the corresponding intra- and intermolecular Fock submatrices is discussed in detail in Ref. 2. The theory described in this reference has been adopted in the present calculations subject to the following approximations:

(1) All integrals involving four different molecules are neglected. This is a good approximation for hydrogen bonded crystals because their open lattices contain only quartets of molecules where at least two intermolecular contacts are relatively long. This is presently regarded as a permanent approximation to be retained for all hydrogen bonded crystals.

(2) All integrals involving three different molecules are also presently neglected. This too is a reasonable approximation for the open hydrogen bonded lattice. However, it is intended to include these integrals in later work on other types of crystal. Much of the algorithm necessary for this purpose has already been programmed.

The neglect of the above molecular integrals does not entirely eliminate three molecule interactions from the theory. These interactions are implicitly included through the coupling between the SCF submatrix equations and explicitly in the calculation of the second order contributions to the crystal density matrix.

(3) All integrals involving molecules up to the third nearest neighbors are calculated exactly. Integrals involving molecules beyond this cutoff point, but still within a sphere of 30 Å radius, are calculated by a dipole expansion about the molecular center of nuclear charge and included into the Fock submatrices by means of dipole lattice sums.

UNIT CELL ELECTRON DENSITIES

Consider a crystal composed of N unit cells each with z molecules and n_e electrons. If D and S are, respectively, the full crystal density and overlap matrices,

the total number of electrons in the crystal lattice will be given by

$$\text{Tr } DS = Nn_e, \quad (2)$$

where Tr is an abbreviation for trace. By taking advantage of the order chosen for the basis set, this equation can be partitioned into inter- and intramolecular submatrices:

$$\sum_P \sum_u \sum_Q \sum_v \text{Tr } {}^P u Q v D {}^P u Q v S = Nn_e. \quad (3)$$

Here Pu labels the molecule which occupies the u th site in the P th unit cell and ${}^P u Q v D$ is an intermolecular density submatrix between two such lattice molecules. The double summation over unit cells in this equation can be reduced to N times a single summation by virtue of the translational symmetry

$$\sum_u \sum_Q \sum_v \text{Tr } {}^P u Q v D {}^P u Q v S = n_e. \quad (4)$$

P in this equation may be regarded as the label for the chosen reference unit cell and Eq. (4) as giving the number of electrons associated with this cell. This suggests that the electron density to be associated with the u th molecule in this cell is given by

$${}^u Q_e = \sum_Q \sum_v \text{Tr } {}^P u Q v D {}^P u Q v S. \quad (5)$$

The double summation over unit cells Q and sites v includes all the molecules in the crystal.

For crystals composed entirely of crystallographically equivalent molecules, intermolecular charge transfer is symmetry forbidden and ${}^u Q_e$ must, therefore, balance the total nuclear charge on the u th molecule. For crystals where intermolecular charge transfer is symmetry allowed, the unit cell remains electrically neutral and under these circumstances it is the sum of ${}^u Q_e$ over all unit cell molecules which must balance the total nuclear charge of the unit cell.

THE CRYSTAL DIPOLE MOMENT

We start by first deriving an expression for the dipole moment m per unit cell of the crystal. If M is the full crystal dipole moment matrix calculated with respect to global crystal axes within the crystal lattice, then the unit cell dipole moment is given by

$$m = \frac{1}{N} \left\{ \text{Tr } DM + \sum_P \sum_\alpha {}^P Z_\alpha R_\alpha(P) \right\}, \quad (6)$$

where Z_α is the nuclear charge of the α th atom in the P th unit cell and $R_\alpha(P)$ is the position vector for the same atom. The density and dipole matrices are next partitioned into inter- and intra-unit cell submatrices

$$m = \frac{1}{N} \left\{ \sum_P \sum_Q \text{Tr } {}^P Q D {}^P Q M + \sum_P \sum_\alpha {}^P Z_\alpha R_\alpha(P) \right\}. \quad (7)$$

As it stands, this equation cannot be simplified by means of the translational symmetry because the dipole submatrices are not translationally invariant. They can be made so by transforming them to local coordinate systems centered within the reference unit cell P of

each submatrix

$$m = \frac{1}{N} \left\{ \sum_P \sum_Q \text{Tr}^{PQ} D ({}^{PQ} M_{\text{local}} - R_P {}^{PQ} S) + \sum_P \sum_\alpha Z_\alpha (R_P + r_\alpha) \right\}, \quad (8)$$

where R_P is the position vector of the P th unit cell relative to the global axes. The translationally invariant component in the above equation $R_P {}^{PQ} S$ cancels part of the nuclear term because of the overall neutrality of the unit cell, and the above equation simplifies to

$$m = \sum_Q \text{Tr}^{PQ} D {}^{PQ} M_{\text{local}} + \sum_\alpha Z_\alpha r_\alpha. \quad (9)$$

Here the summation over Q includes all unit cells in the crystal and the summation over α includes all the atoms within the reference unit cell.

If there is only one molecule per unit cell its dipole moment is given by

$$m = \left(\text{Tr}^{PP} D {}^{PP} M_{\text{local}} + \sum_\alpha Z_\alpha r_\alpha \right) + \sum_Q' \text{Tr}^{PQ} D {}^{PQ} M_{\text{local}}. \quad (10)$$

The first term gives the intramolecular contribution to the dipole moment and includes the effects arising from the polarization of the lattice molecules by the crystal field. The second term gives the intermolecular contribution arising from the partial delocalization of electrons from the reference lattice molecule onto its neighbors.

If there is more than one molecule per unit cell Eq. (9) may be usefully expanded further by partitioning the unit cell submatrices into inter- and intramolecular submatrices and transforming the dipole moment submatrices to axes centered on their reference molecule. The expanded expression for the unit cell dipole moment is given in Eq. (11),

$$m = \sum_u ({}^u Q_n - {}^u Q_e) \tilde{u} + \sum_u \left[\left(\text{Tr}^{PuPu} D {}^{PuPu} M_{\text{local}} + \sum_\alpha {}^u Z_\alpha r_\alpha \right) + \sum_Q' \sum_v \text{Tr}^{PuQv} D {}^{PuQv} M_{\text{local}} \right], \quad (11)$$

where ${}^u Q_n$, \tilde{u} , and ${}^{PuQv} M_{\text{local}}$ are, respectively, the total nuclear charge and unit cell position vector of the u th molecule and the intermolecular dipole moment matrix calculated with respect to axes centered on the reference molecule Pu .

TABLE I. Atomic coordinates, in atomic units, for solid HF and HCl. The a coordinates are zero.

Atom	H-F		H-Cl	
	b Axis	c Axis	b Axis	c Axis
H	3.574304	0.355117	1.726128	0.773466
X	2.012558	1.242911	0.0	2.387242

TABLE II. Pairs of molecules in the solid HF and HCl. All distances are in atomic units.

Contact number	Number of molecules	Shortest distance HF/HCl
1	2	2.936/4.606
2	4	5.193/6.577
3	4	5.346/6.642

Clearly for crystals where all molecules are crystallographically equivalent there can be no charge transfer, the first term in the above equation is zero and the quantity in the square bracket defines the molecular dipole moment. However, when the first term does not vanish, the dipole moment of a given molecule is not well defined, and only the total unit cell moment can be calculated. The first term gives the charge transfer contribution to the unit cell dipole, and the second two give, respectively, the intra- and intermolecular contributions to this moment.

If the dipole moment of the lattice molecules is zero, Eq. (11) can be used, with appropriate modifications to M_{local} and the nuclear contribution, to calculate the next higher electric moment. However, this equation cannot be used as it stands to calculate moments higher than this, since their origin dependence invalidates the derivation of Eq. (9) from Eq. (8).

STRUCTURAL DATA FOR SOLID HF AND HCl

The structural data reported for solid HF⁵ and HCl⁶ were used for all of the calculations reported here. Both molecules crystallize in the same orthorhombic space group $Bm2_1b$ in which there are four symmetry related molecules per unit cell. These molecules form part of two parallel zigzag chains which pass through each unit cell parallel to the b axis. The main structural difference between the two crystals is in the orientation of the molecules within these chains and in their closest intermolecular contacts. The chain angle for HF is 116° and the hydrogen bonding distance is 1.5 \AA . The corresponding data for HCl are 93° and 2.4 \AA , respectively. The atomic coordinate for the reference molecule in both crystals are given in Table I.

The intermolecular matrices involving all pairs of molecules making intermolecular contacts of up to, 5.5 and 6.7 a.u., respectively, for HF and HCl were explicitly calculated. The number of pairs found using these discriminants was ten for both crystals, see Table II. A double scan of these pair lists provides a list of triplets of molecules necessary for the second order calculation and eventually the inclusion of three-molecule integrals. In the present calculation the list of triplets is limited to those for which the longest intermolecular contact is no greater than the pairs discriminant: 24 triplets were found for both crystals.

The basis set used for both crystal calculations is 3-21G.^{7,8}

TABLE III. Calculated molecular dipole moment for solid HF in atomic units. The a axis component is zero by symmetry.

Contribution	b Axis	c Axis
Zero intramolecular	0.7947	-0.4518
Intramolecular	-0.0591	0.0091
Intermolecular	-0.0741	0.1313
Total	0.6615	-0.3114

TABLE IV. Calculated molecular dipole moment for solid HCl in atomic units. The a axis component is zero by symmetry.

Contribution	b Axis	c Axis
Zero intramolecular	0.5281	-0.4937
Intramolecular	-0.0190	0.0775
Intermolecular	-0.0120	-0.0304
Total	0.4971	-0.4466

TABLE V. Calculated molecular quadrupole moments for solid HF in atomic units. The components not listed are all zero by symmetry.

Contribution	$a^2 - b^2$	$3c^2 - r^2$	bc
Zero intramolecular	-1.7399	-0.2051	-1.4304
Intramolecular	0.0694	0.0009	0.0171
Intermolecular	0.7423	0.0791	0.1373
Total	-0.9282	-0.1251	-1.2760

TABLE VI. Calculated molecular quadrupole moment for HCl in atomic units. The components not shown are all zero by symmetry.

Contribution	$a^2 - b^2$	$3c^2 - r^2$	bc
Zero intramolecular	1.8778	0.4683	-2.8509
Intramolecular	-0.1789	-0.0519	0.0030
Intermolecular	0.0380	-0.0038	0.0488
Total	1.7369	0.4126	-2.7991

CALCULATED DIPOLE AND QUADRUPOLE MOMENTS

The quadrupole moment is not the first nonvanishing momenta of either HF or HCl and is therefore origin dependent. Consequently, Eq. (9) cannot be used strictly to calculate the molecular quadrupole moments of these crystals. Although the quantity calculated from Eq. (9) cannot be taken as an accurate value for

the crystal quadrupole moment, it does give some measure of the crystal field's effect on the molecular charge distribution and has accordingly been calculated and reported here.

The molecular dipole moments calculated for HF and HCl in their crystal lattices are given in Tables III and IV, respectively. The magnitude of the moment calculated for HF is 0.731 a.u. which indicates a slight decrease for the crystal when it is compared with the corresponding theoretical⁷ free molecule value of 0.854 a.u. Moreover, this change is largely due to the increase in the HF bond length observed in the solid state. Qualitatively similar results are found for solid HCl: the theoretical crystal dipole moment is 0.668 a.u. which is only marginally different from the corresponding theoretical⁸ free molecule value of 0.693 a.u.

Interestingly, qualitatively similar results⁹ were obtained from CNDO based calculations for solid HF and a wide variety of other hydrogen bonded crystals. Estimates of molecular dipole moments based on experimental unit cell charge distribution also yield relatively small changes.¹⁰ Thus it would appear that while the hydrogen bonding within the crystal causes an appreciable polarization of the molecular charge distribution, it does so in such a manner as to produce a relatively small change in the dipole moment.

The calculated estimates of the molecular quadrupole moments for solid HF and HCl are given in Tables V and VI, respectively. Although the crystal induced changes are slightly larger for these moments, they amount to only about 20% in most cases. The interesting feature of these results is the relatively large contribution from the intermolecular terms which show that changes to the outer region of the molecular charge distribution resulting from the hydrogen bonding crystal interaction are appreciable.

DISCUSSION

In view of the novel method of calculation used here, it is appropriate at this point to discuss some of its practical aspects.

The convergence of the CNDO based version of the present theory has been discussed, from both the point of view of the iterative cycles and the perturbative series, in detail elsewhere.^{11,12} The convergence of the SCF cycles is better, at least in the cases of HF and HCl with minimal and 3-21G basis, than that of the CNDO calculations. This is particularly encouraging since under the CNDO approximation the symmetry of the solids discussed here is sufficient to decouple all of the matrix equations, whereas at the *ab initio* level these equations remain strongly coupled. The convergence with respect to perturbative series of the *ab initio* calculations closely parallels that reported for the CNDO theory.

All of the calculations reported here were carried through using the crystal program package CRYPT soon to be submitted to QCPE. The integral evaluation codes were all taken from the POLYATOM package.¹³

- ¹P. Coppens and E. D. Stevens, *Advances in Quantum Chemistry* (Academic, New York, 1977).
- ²S. F. O'Shea and D. P. Santry, *Theor. Chim. Acta* **37**, 1 (1975).
- ³D. P. Santry in *The Electronic Structure of Molecular Crystals, NATO Advanced Summer Institute on Molecular Crystals and Polymers* (Plenum, New York, 1975).
- ⁴C. C. J. Roothaan, *Rev. Mod. Phys.* **23**, 69 (1951).
- ⁵M. W. Johnson, E. Sandor, and E. Arzi, *Acta Crystallogr. B* **31**, 1998 (1975).
- ⁶E. Sandor and M. W. Johnson, *Nature* **217**, 541 (1968).
- ⁷J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.* **102**, 939 (1980).
- ⁸M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, and W. J. Hehre, *J. Am. Chem. Soc.* (to be published).
- ⁹D. P. Santry, *Chem. Phys. Lett.* **27**, 464 (1974).
- ¹⁰E. D. Stevens and P. Coppens, *Acta Crystallogr. B* **36**, 1864 (1980).
- ¹¹J. Bacon and D. P. Santry, *J. Chem. Phys.* **55**, 3743 (1971).
- ¹²D. P. Santry, *Theoret. Chim. Acta (Berlin)* **42**, 67 (1977).
- ¹³POLYATOM Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.