

Padé Approximation to the Infinite Number of Point Charge Shells in Madelung Potential Affected Cluster Calculation of Molecules

The Comparison with the Crystal Orbital Method

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Charge distribution and the total energy of a CO molecule in the crystalline α -carbon monoxide has been calculated by the *ab initio* method within the 6-31G basis. Two approaches to this problem have been compared: calculation using the crystal orbital method and the cluster calculation considering one molecule and respecting the crystal environment by electrostatic approximation, using the model of point charges. It turned out that the electrostatic approximation supplemented by the Padé's extrapolation for infinite crystal dimensions, leads to a very good agreement with results obtained by the crystal orbital method. The advantage of the proposed approach is its general applicability to any kind of structure, in contrast to traditional Ewald techniques.

Two basic approaches have been established to the quantum-chemical treatment of extended systems. The first one consists of crystal-orbital-type methods [1–4]. These methods, describing solids with the exact translational symmetry are considered as standard in the electronic structure calculations of three-dimensional crystalline solids. Various methodological procedures are being applied depending on the nature of the problem studied. There exist quite successful attempts to adopt this method to describe amorphous and disordered systems and to study defects of the crystal structure. The unit cell is chosen large enough to include a whole set of disordered atoms and results are related to the system of periodically repeated unit cells [5]. In the case of crystal structure defects (impurities in crystals, colour centres, vacancies, etc.) the unit cell is chosen according to the concentration of the crystal perturbation [6].

In spite of the success of the above-mentioned methods the cluster approach is still used in electronic structure calculations of solids and it has its own fields of application. Good examples of this approach to electronic structure study of transition metal compounds are the works [7–10] and references cited therein. A complex ion as the prototype molecule and/or clusters representing a part of continuous structure are investigated here. Papers studying the influence of the surroundings on the transition metal ion itself have appeared [11]. Some modified cluster methods are used in investigating molecular crystals [12, 13], proton conductivity, defects and impurities in crystals [14]

and modelling of acidic sites of zeolites [15]. Theoretical studies attempting to include effects of the surroundings on the electronic structure of simple ions, of which the crystal consists, also belong to the cluster approach group ([16] and references therein).

A variety of reasons justify the use of cluster methods. The main reason is that the delocalized description provided by crystal-orbital-type methods does not represent a good base for the calculation of the localized properties of crystals [17]. Most of the cluster approaches include the effect of surroundings into the Hamiltonian to the various degree of approximation. Such approximation is equivalent to the crystal-orbital calculation in the Γ point of the k space, and its great advantage is the direct space representation of the wavefunction which is simpler to interpret. This procedure was applied to covalent clusters in Ref. [18]. Later, the method of molecular cluster embedded into the infinite crystal has appeared [19].

Heterodesmotic crystals, molecular and/or ionic, represent the case of strictly localized electrons, where the cluster approach is fully justified. The strongest interaction here is the electrostatic interaction, which is the long-range one as well. This fact originated several methods based on purely electrostatic approximation to the effect of surroundings on the cluster studied. Detailed analysis of such procedures is given by *Ángyán* in [13]. Noteworthy is his finding that the effective Schrödinger equation obtained in this way is formally equivalent to the nonlinear Schrödinger equation.

tions used in average reaction field theories of solvent effect. This has encouraged us to apply electrostatic models in amorphous system studies [20].

Although both approaches, crystal-orbital-type methods and cluster methods, are widely used in electronic structure calculations of solids, the direct comparison of these two main approaches is still missing. The goal of this paper is to confront them for the case of small covalent system. A new extrapolation procedure for the infinite number of point charge shells is tested at the same time.

METHOD

The effect of the crystal structure on the electronic structure of a molecule is represented by electrostatic interactions. The influence of point charges from a crystal environment is included into the molecular Hamiltonian

$$\mathcal{H} = \mathcal{H}^{\circ} + \sum_i^{N_q} \sum_j^{N_e} \frac{q_i e^2}{R_{ij}}$$

where \mathcal{H}° is the Hamiltonian of the isolated molecule, q_i stands for the i -th point charge, R_{ij} is written for the distance from the point charge i to the electron j , N_q , N_e and e are number of point charges, number of electrons and elementary charge, respectively. In the self-consistent charge

iterative procedure the starting point charge set is taken from *in vacuo* calculation, similarly as in [13, 21]. The choice of the point charge set is done in analogy with [18]. This set is divided into shells, the first of them consists of the point charges contained in the chosen unit cell neighbouring to the molecule (Fig. 1), the second shell was represented by point charges contained in unit cells surrounding the first shell, etc. (the total number of unit cells in n shells is $(2n - 1)^3$).

The unit cell (Fig. 1) is chosen in such a way as to have the same symmetry as is the symmetry of the ideal crystal (the lowered symmetry could cause additional nonphysical polarization). This unit cell is larger than the crystallographic one. Its replication in the space along translation vectors causes that some positions are occupied twice or more, so the calculation procedure which increases number of shells contains a check for redundant positions. Only one molecule is then considered in one position of the space.

The electronic structure of the system with the infinite number of shells was obtained by means of an extrapolation procedure. Padé approximants $P(i, j)$ (for definition of the used symbols see the Appendix) are used to extrapolate calculated quantities. The consistency of this procedure was tested by means of the semiempirical CNDO method [22]. Two sets of quantities are compared here. The first of them is obtained using Padé approximant extrapolation for the number of shells $n = 1, 2, 3, 4,$ and 5. The second one is a result of the cluster

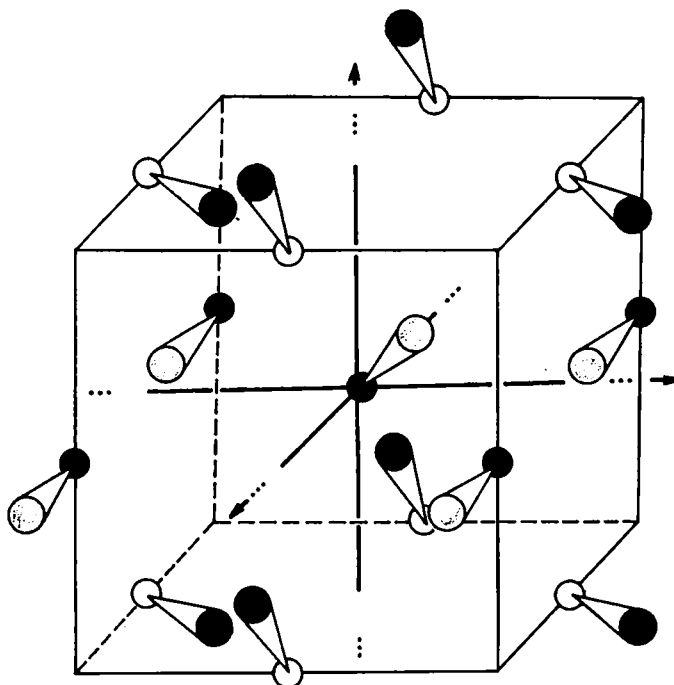


Fig. 1. The unit cell chosen for the electronic structure calculation of α -carbon monoxide molecule. All molecules except the central one are replaced by point charges. ● Carbon, ○ oxygen.

calculation with modified diagonal elements of CNDO Hamiltonian. These were corrected for the interaction with point charge shells by means of Padé approximants.

α -Carbon monoxide crystal was chosen as a testing system. It represents a molecular crystal in which the cluster calculation of the electronic structure is justified. Consequently, if any discrepancies will occur they have to be ascribed to the crudeness of electrostatic interaction approximation and/or to the Padé approximant extrapolation scheme. The only condition for the testing procedure to be efficient is the choice of polar testing system (if it is homomolecular) and α -carbon monoxide crystal fulfils this condition.

Moreover, the carbon monoxide molecule is known to belong to the group of problematical systems from the point of view of the Hartree–Fock method. In these systems a break-down of Koopmans theorem occurs and SCF procedure results in the bond polarity of the opposite sign [23]. It is therefore interesting to find out how these systems will behave after taking into account the effect of surroundings though on the electrostatic level only.

The experimental geometry [24] was used in our calculations. The surrounding medium effects restricted to the electrostatic interaction do not guarantee the correct prediction of the system geometry, but the well known geometry supplied by point charges effects enables us to obtain electronic structure details of reasonable accuracy [13].

RESULTS AND DISCUSSION

The elementary unit of α -carbon monoxide crystal is primitive cubic. It contains four molecules and belongs to the space group $P2_13$ [24]. For the purpose of the outlined calculations we have chosen the cubic unit cell with one molecule in its centre surrounded by other twelve molecules placed in the centres of edges. Point charges taken instead of these twelve neighbouring molecules represent the first shell. The symmetry of such unit cell is the same as the symmetry of the crystal (Fig. 1). The coordinates of atoms in the unit cell together with the structural data are collected in Table 1.

Table 2 presents the total energies, core–lattice interaction energies and net carbon charges $q(C)$ calculated for CO molecule *in vacuo* and/or surrounded by 1, 2, and 3 shells of point charges. The table is completed by crystal orbital approach results [25] and by two Padé approximants of these three quantities. Both calculations, cluster approach and crystal orbital one are accomplished on *ab*

Table 1. The Coordinates of Atoms in the Cell Chosen for Computation

Atom	x	y	z	Atom	x	y	z
C	0	0	0	O	$-b-\beta$	$-\beta$	$b+\beta$
O	β	β	β	C	b	0	$-b$
C	b	b	0	O	$b-\beta$	$-\beta$	$-b+\beta$
O	$b+\beta$	$b-\beta$	$-\beta$	C	$-b$	0	$-b$
C	$-b$	b	0	O	$-b-\beta$	$-\beta$	$-b+\beta$
O	$-b+\beta$	$b-\beta$	$-\beta$	C	0	b	b
C	b	$-b$	0	O	$-\beta$	$b+\beta$	$b-\beta$
O	$b+\beta$	$-b-\beta$	$-\beta$	C	0	$-b$	b
C	$-b$	$-b$	0	O	$-\beta$	$-b+\beta$	$b-\beta$
O	$-b+\beta$	$-b-\beta$	$-\beta$	C	0	b	$-b$
C	b	0	b	O	$-\beta$	$b+\beta$	$-b-\beta$
O	$b-\beta$	$-\beta$	$b+\beta$	C	0	$-b$	$-b$
C	$-b$	0	b	O	$-\beta$	$-b+\beta$	$-b-\beta$

Lattice constant $a = 0.563$ nm, $b = a/2 = 0.2815$ nm, $\beta = 0.0615$ nm ($\beta = \text{bond length}/\sqrt{3}$).

initio level using 6-31G basis set which is equivalent to the double-zeta Slater-type orbitals (STO) [26]. Crystal orbitals are calculated for Γ point of the k space. In such a case the electronic structure of the α -carbon monoxide molecule is influenced by the nonlocal potential originated from all the other molecules positioned in the rest of the infinite crystal.

Table 2. Results of *ab initio* Computations of Electronic Structure of Solid α -Carbon Monoxide (6-31G Basis Set)

Computation method	Total energy/eV	Core–lattice	
		interaction energy/eV	$q(C)/e$
<i>in vacuo</i>	-3062.7665	0.0	0.381
1 shell	-3062.8710	4.7853	0.426
2 shells	-3062.8691	4.3164	0.422
3 shells	-3062.7687	4.1502	0.421
Crystal orbital	-3062.8623	not computed	0.406
P(2, 0)	-3063.7687	4.1502	0.421
P(1, 1)	-3062.8710	4.0588	0.420

As reported in Table 2 the CO bond polarity is correct even in the *in vacuo* case. Two factors are supposed to cause this result: the standard split valence basis set (the opposite direction of the dipole moment of CO molecule appears near Hartree–Fock limit) and molecular geometry. The bond length 0.1065 nm used in our calculations of the CO crystal is far from that of free molecule which is 0.112 82 nm [27].

By inclusion of point charge spheres into the calculated system the polarity of the CO bond increases. The carbon net charge raises from 0.381 e to 0.420 e. The only one shell considered causes its overestimation but every next shell taken into account makes it lower. The crystal orbital carbon net charge is 0.406 e. The electrostatic approximation result extrapolated to the value for infinite

number of shells is thus higher by the value 0.014 e. This effect is apparently related to the neglect of the intermolecular electron—electron interaction and it should be expected that in cluster calculation of homodesmotic full covalent systems this interaction should not be neglected. The correspondence achieved in carbon net charges obtained by two methods – the crystal orbital approach and the Padé approximants P(1, 1) to the cluster results – shows the applicability of the purely electrostatic approximation to the molecular crystals.

The molecular orbital energy levels are not significantly affected by taking into account the effect of surroundings in the electronic structure calculation. The inclusion of the point charges shifts the energy levels slightly to the lower values (by hundredth of eV). The energy difference of the highest occupied and the lowest unoccupied molecular orbital increases only by ca. 0.02 eV when going from molecule *in vacuo* to the molecule embedded in a point charge environment (the change of the real transition from the gas phase to the crystalline one is not considered).

The total energy obtained by means of crystal orbital method differs from Padé approximant P(1, 1) by a value of 0.01 eV. This coincidence is rather surprising owing to the fact that electron—electron interactions between neighbouring molecules are completely neglected in the latter case.

The core—lattice interaction energy estimated by Padé approximant P(1, 1) is 4.0588 eV. Contrary to the destabilization effect of this interaction, the electron—lattice interaction energy amounts to 4.16 eV (compared to electron energy of the *in vacuo* molecule with the same geometry). The formalism of the crystal orbital method does not allow to calculate these interaction energies.

The problem whether the Padé approximant me-

thod contains contradictory features has been questioned by using the CNDO method. Two reasons exist for the choice of this semiempirical method. The first one is the simplicity and straight applicability of the method. The electrostatic effect concerns here only diagonal elements of the Hamiltonian. The second reason is that semiempirical quantum-chemical methods are still being applied to the large clusters (e.g. simulation of amorphous systems) and to the transition metal coordination complex calculations. Therefore it seems to be interesting to verify how such large systems behave when affected by point charge surroundings.

Table 3 collects the diagonal elements corrections $V(C)$ $\{V(O)\}$ of the Fock matrix corresponding to the carbon or oxygen atomic orbitals, the total electronic energy, net carbon charges and Wiberg indices $W(C—O)$ [28] of the CO bond for the number of shells $n = 0, 1, \dots, 5$. Next two rows represent Padé approximants P(4, 1) and P(3, 2) of these quantities. The table is completed by the results obtained using Padé approximants to the diagonal corrections.

Although the Wiberg index is not actually affected by the number of the point charge shells, the change in the total electronic energy is at the SCF threshold on going beyond the number of shells $n = 4$.

The full coincidence is achieved between the results obtained by means of the Padé approximants to the diagonal corrections and Padé approximants to the total electronic energy and net carbon charge. This result implies that it does not matter whether Padé extrapolation scheme is applied to the calculated quantity or to its diagonal correction term. This fact enables us to construct more effective calculation algorithm in which the SCF procedure is used only Nit -times instead of $Nit \cdot n$ -times (Nit stands for the number

Table 3. Results of CNDO Computations of Electronic Structure of Solid α -Carbon Monoxide

Method	$V(C)/eV$	$V(O)/eV$	Total electronic energy/eV	$q(C)/e$	$W(C—O)$
<i>in vacuo</i>	0.0	0.0	- 679.40956	0.000987	2.6528
1 shell	- 0.00001704	0.00901405	- 679.41858	0.001068	2.6527
2 shells	- 0.00001256	0.00118582	- 679.41663	0.001050	2.6528
3 shells	- 0.00001192	0.00121108	- 679.41678	0.001052	2.6527
4 shells	- 0.00001173	0.00121699	- 679.41682	0.001052	2.6527
5 shells	- 0.00001166	0.00121944	- 679.41683	0.001052	2.6527
P(4, 1)	- 0.00001160	0.00122117	- 679.41684	0.001052	2.6527
P(3, 2)	- 0.00001139	0.00123727	- 679.41694	0.001052	2.6527
Diagonal correction	-	-	- 679.41684	0.001052	2.6527
P(4, 1) Diagonal correction	-	-	- 679.41694	0.001053	2.6527

of iterations and n represents the number of shells).

CONCLUSION

We have demonstrated the consistency of the Padé extrapolation scheme at the semiempirical CNDO level. This method is successfully used to extrapolate quantities obtained by electronic structure calculation of the molecular cluster of carbon monoxide embedded in a point charge environment to the infinite number of point charge shells. The Padé approximation scheme is a general purpose method. Contrary to the Ewald formulae for the Madelung sums it is applicable to any type of lattice. In the case of highly asymmetric systems the need for the higher number of shells should be expected for correct description of the charge density redistribution.

The results of the *ab initio* calculations of the same system show that electrostatic approximation to the crystal environment causes a little higher polarity of the C—O bond than that by the crystal orbital method. The difference in charge distribution obtained by these two methods enables the application of the electrostatic approximation to the covalent crystals. This approximation completed with Padé extrapolation scheme results in the total energy, which is in good agreement with that one by the crystal orbital method.

APPENDIX

In the method of Padé approximants [29] an infinite element of a series of $k + 1$ elements $f_1, f_2, f_3, \dots, f_{k+1}$, which is supposed to be convergent, is calculated in the form of polynomials $P(k, 0), P(k - 2, 2), \dots, P(0, k)$, where

$$P(i, j) = \sum_{p=0}^i a_p / \sum_{r=0}^j b_r$$

The coefficient b_0 obeys the rule $b_0 = 1$ and indices i and j are connected by the relation $i + j = k, i \geq j, j \geq 0$. The detailed calculation procedure for obtaining coefficients a_p and b_r is described in [29].

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