Theor Chim Acta (1986) 70: 227–236

Theoretica Chimica Acta

Ab initio SCF calculations of the linear infinite chain of LiH according to the pseudo-lattice method

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(Received April 25/Accepted June 2, 1986)

The pseudo-lattice (PL) method has been reformulated for *ab initio* self-consistent-field (SCF) calculations. The translational symmetries of infinite systems have been applied to the finite model chain by manipulating all the intramolecular and intermolecular Fock matrices. The nuclear repulsion energy has been corrected accordingly. The method has been tested for the linear chain of lithium hydride under the constraint of equidistance between all neighboring lithium and hydrogen atoms. The calculated results of the infinite chain have been compared with those of finite chains of lithium hydride under the same geometric constraint. The equilibrium geometries, band structures, intermolecular stabilization energies and potential curves have been studied. It is found that the infinite systems cannot be described by considering only first nearest neighbor interactions, and the intermolecular interactions must be considered at least up to third nearest neighbors in order to obtain accurate value of force constant of infinite systems. We can conclude from band structures of infinite chains that the boundary effect of the finite model chain is effectively removed by the PL method.

Key words: Infinite Chain — Pseudo-lattice method

1. Introduction

Various methods have been employed for the study of the electronic structures of polymers and molecular crystals [1–15]. Among them, the small periodic cluster (SPC) method [10, 11] and the PL method [12–15] utilize the translational symmetry of Born–von-Karman cells or elementary molecules of crystals. The SPC method has been applied to the study of point defect problems of hexagonal-layered solids [10] and the electronic structure of solid hydrogen fluoride [11]. The PL method has been used to study the stability of various forms of ice [12], hydrogen bond energy of solid hydrogen fluoride [13], geometries of polymeric berillium hydride, polyethylene and polymeric boron hydride [14], and lattice vibration of A type zeolite [15]. The results of both SPC and PL methods were in reasonable agreement with other types of calculations such as crystal orbital (CO) method for molecular crystals. However, the previous applications of SPC and PL methods are all based upon semiempirical SCF methods [16], and no attempt have been made to extend the methods into *ab initio* calculations. In this work, we present the treatment to use the PL method in *ab initio* calculations.

In the semiempirical treatment, all two-electron integrals involving three- and four-centers are neglected and the imposition of the translational symmetry is rather simple. In the *ab initio* treatment, the neglects of three- and four-center integrals are not inherent in the theory and the extra considerations are required in order to impose the translational symmetry. Therefore, the PL calculation using *ab initio* SCF method is slightly more complicated than one using the semiempirical computation, but offers considerable advantages in terms of accuracy and the potential for improvement.

In this paper, we reformulate the PL method for *ab initio* calculations of linear chains of identical molecules for the reason of simplicity. Test calculations are performed for the linear chain of lithium hydride. Lithium hydride is well suited for the test purpose since many theoretical results are available for the structures and stabilities of lithium hydride clusters [17–22].

In the following sections, we describe the formalism and calculational method for the *ab initio* PL treatment and the results of actual calculations for LiH chain.

2. Theory and method of calculation

A polymer or molecular crystal is a collection of repeating unit cells or molecules with a certain translational symmetry. The aim of the PL method is to represent a crystal by this repeating unit cell which is usually a cluster of molecules. The PL method using *ab initio* SCF calculations is illustrated on a one-dimensional linear chain of identical molecules for simplicity, but extensions to more general shapes of clusters are not expected to cause any serious difficulties.

Let us suppose that our model chain is composed by $2N+1$ identical molecules and each molecule is made up by n atoms. If each molecule is expressed by m basis functions in the Fock equation, the total number of basis functions in the equation for the model chain is $(2N+1)m$ and the total number of matrix elements in the Fock matrix F is $(2N+1)m\times(2N+1)m$. This F matrix can be arranged as $(2N+1)\times(2N+1)$ submatrices (Fig. 1) where the diagonal submatrices are intramolecular Fock matrices and other off-diagonal submatrices are intermolecular ones. These submatrices are denoted as $H(I,J)$'s which represent the interactions between Ith and Jth molecules in the chain. The edge

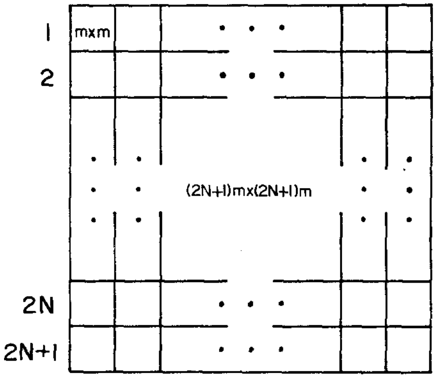

Fig. 1. Submatrix notation for the Fock matrix of the model chain composed by $2N+1$ molecules. The dimensions of matrices are shown

effect of clusters appears in both intramolecular and intermolecular submatrices. Since the matrix is symmetric for the usual choice of real matrix representations, we only limit our attention to the lower triangular part of the matrix.

According to the translational symmetry of the elementary molecules in the chain, the molecules (A and B) at boundaries of the model chain are translated to the outside of other boundaries (A' and B', Fig. 2). This operation adds each $2N+1$ molecules to both sides of the model chain by the translational symmetry of repeating unit cells. In order to incorporate the translational symmetry of the infinite chain to model chain of finite size, both the diagonal and off-diagonal submatrices must be modified.

All the diagonal submatrices are substituted by $(N+1)$th diagonal submatrix,

$$H(I, I) = H(N+1, N+1) \tag{1}$$

for all I's of $1 < I < 2N+1$ because among the molecules in the model chain, $(N+1)$th molecule has the most similar environment to the molecule in the infinite chain.

The off-diagonal submatrices are classified into two groups according to the interaction orders or distances between molecules. One group, group (i), contains off-diagonal submatrices with the intermolecular interaction order less than or equal to N. Other off-diagonal submatrices belong to group (ii) as shown in Fig. 3. For the submatrices of group (i), all $H(I+k, I)$'s of $1 < I < 2N+1$ for a given k are substituted by their central submatrix which is most suitable for expressing the intermolecular interactions in the infinite chain. Following relationship,

$$H(I, J) = H(I+k, J+k) \tag{2}$$

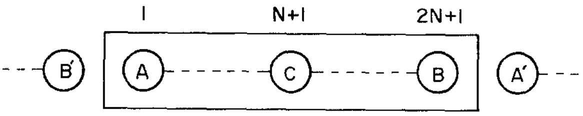

Fig. 2. Translations of the molecules A and B at the boundaries of the model chain

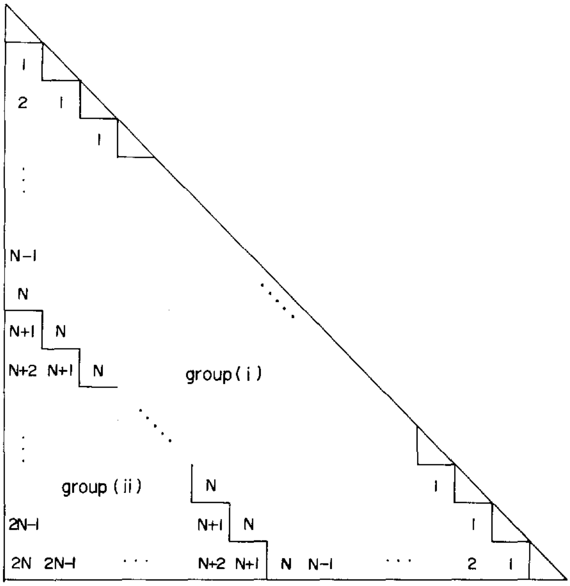

Fig. 3. Classification of the off-diagonal submatrices. The numbers in the Fock matrix represent the intermolecular interaction orders of corresponding submatrices

for any integers I, J and k, is satisfied for the diagonal and off-diagonal submatrices of group (i) after the successive above operations. For the off-diagonal submatrices of group (ii), the translational symmetries of elementary molecules and the repeating unit cells must be carefully applied. If we define the translational operator T as

$$R_{A'} = T_{AA'} R_A \tag{3}$$

where R_A and $R_{A'}$ are the positions of molecule A and A' respectively, the interaction between molecules A and B is replaced by that of A' and B so that the matrix element of the Fock matrix F for the interaction between the basis functions μ on molecule A and ν on B is given as

$$\begin{aligned} F_{\mu\nu} &= F_{\mu'\nu} \\ &= h_{\mu'\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu'\nu|\lambda\sigma) - \tfrac{1}{2}(\mu'\lambda|\nu\sigma)] \end{aligned} \tag{4}$$

where μ' is the atomic orbital on molecule A' and all other symbols have their usual meanings. The overlap integral becomes likewise

$$\begin{aligned} S_{\mu\nu} &= S_{\mu'\nu} \\ &= \int \mu'(A')\nu(B)\, d\tau \end{aligned} \tag{5}$$

These are transformations for the first nearest neighbor interactions at the right boundary of the model chain (see Fig. 2), and those for other interactions in group (ii) are straightforward.

As the result of all the above operations, the total amount of electronic energy for each molecule in the model chain corresponds to the situation where N molecules are located at left and right sides of the molecule respectively (Fig. 4). Therefore, the nuclear repulsion energy must be modified accordingly. The corrected total nuclear repulsion energy ($E^{\mathrm{tot}}_{\mathrm{rep}}$) is given by

$$\begin{aligned} E^{\mathrm{tot}}_{\mathrm{rep}} &= E^{M}_{\mathrm{rep}} + E^{\mathrm{corr}}_{\mathrm{rep}} \\ &= \frac{1}{2} \sum_{i=1}^{n(2N+1)} \sum_{j=1}^{n(2N+1)} \frac{Z_i Z_j}{R_{ij}} + E^{\mathrm{corr}}_{\mathrm{rep}} \end{aligned} \tag{6}$$

where E^{M}_{rep} refers to the original nuclear repulsion energy of the model chain, $n \times (2N+1)$ is the number of atoms in the model chain, Z_i and Z_j are the nuclear charge of atoms i and j, R_{ij} is the distance between i and j atoms, and $E^{\mathrm{corr}}_{\mathrm{rep}}$ is correctional nuclear repulsion energy for the given condition. $E^{\mathrm{corr}}_{\mathrm{rep}}$ is obtained by

$$\begin{aligned} E^{\mathrm{corr}}_{\mathrm{rep}} &= \tfrac{1}{2} \textstyle\sum_{\alpha=1}^{2N+1} {}^{\alpha}E^{\mathrm{corr}}_{\mathrm{rep}} \\ &= \frac{1}{2} \sum_{\alpha=1}^{2N+1} \sum_{i=1}^{n} \left(\sum_{j \in A(\alpha)}^{l(\alpha)} \frac{Z_i Z_j}{R_{ij}} - \sum_{j \in B(\alpha)}^{l(\alpha)} \frac{Z_i Z_j}{R_{ij}} \right) \end{aligned} \tag{7}$$

where ${}^{\alpha}E^{\mathrm{corr}}_{\mathrm{rep}}$ is the correctional nuclear repulsion energy corresponding to the αth molecule in the model chain, n is the number of atoms in the αth molecule, and $l(\alpha)$ is the number of atoms in the region $A(\alpha)$ or $B(\alpha)$ in Fig. 4. The molecules in the region $A(\alpha)$ are located within the interaction range of the αth molecule while those in the region $B(\alpha)$ are not.

In summary, the following procedures are applied to the Fock matrix F of the model chain in order to imply the translational symmetry of the infinite chain.

Step 1

Intramolecular submatrices. All the intramolecular submatrices $H(x, x)$'s are substituted by $H(N+1, N+1)$ which corresponds to the central molecule in the model chain.

Step 2

Intermolecular submatrices of group (i) *in Fig. 3.* All the intermolecular submatrices of the type $H(x+1, x)$ are substituted by the arithmetic average of $H(N+1, N)$ and $H(N+2, N+1)$ because these submatrices have no central submatrix. The submatrices of the type $H(x+2, x)$ are substituted by their central matrix which is $H(N+2, N)$. All other intermolecular submatrices of group (i) are substituted in these manners.

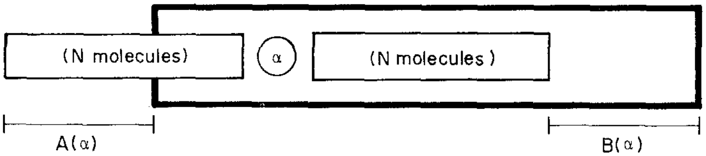

Fig. 4. New environment of αth molecule in the model chain for PL method. The *bold-lined rectangular* represents the model chain

Step 3

Intermolecular submatrices of group (ii) in Fig. 3. At first, $H(2N+1, 1)$ which corresponds to the first nearest neighbor intermolecular submatrix by utilizing the translational symmetry of unit cells in Fig. 2 is substituted by the transpose of one of $H(x+1, x)$'s which have been equalized at second step. Since the interaction geometry is opposite, the transpose is taken. $H(2N, 1)$ and $H(2N+1, 2)$ which correspond to the second nearest neighbor intermolecular submatrices are substituted by the transpose of one of $H(x+2, x)$'s. Other intermolecular submatrices of group (ii) are substituted in the same manner.

Step 4

Nuclear repulsion energy correction. The correction of nuclear repulsion energy is performed according to Eqs. 6 and 7.

3. Calculations

The SCF calculations were carried out using two different basis sets of contracted gaussian type functions (CGTF's) for Li, $9s/3s$ (Basis set I) [23] and $10s/4s$ (Basis set II) [24]. For hydrogen, $4s/2s$ [23] set was used. Although all Li-H distances are same in the crystalline lithium hydride [25], they are not the same for the minimum geometry of the linear $(\text{Li-H})_\infty$ due to the anisotropy of the linear model chain. All PL calculations, however, have been performed under the equidistance constraint since the magnitude of difference in distances is only about 10^{-2} a.u. [21]. The minimum energy geometries of the linear $(\text{LiH})_n$ for $n = 1-5$ were obtained under the equidistance constraint and compared with those of the PL calculations on the $(\text{LiH})_\infty$. The PL calculations have been performed using three different model chains which are composed by three, five and seven molecules of lithium hydride, respectively. The intermolecular stabilization energies have been calculated using the counterpoise (CP) method [26] in order to reduce the basis set superposition error. In the CP method, the energies of subsystems are calculated using all the basis set of the whole composite system [27].

4. Results and discussion

The equilibrium properties of the linear $(\text{LiH})_n$ for $n = 1$-5 obtained under the equidistance constraint are listed in Table 1. Those of the linear infinite chain of lithium hydride, $(\text{LiH})_\infty$, calculated by the PL method are listed in Table 2. The PL calculations with the model chain $(\text{LiH})_3$, which includes only first nearest neighbor interactions, failed to produce minimum energy geometries of $(\text{LiH})_\infty$, implying that more than first nearest neighbor interactions are necessary in the PL method even for the qualitative description of the infinite chain of LiH. The equilibrium bond lengths of $(\text{LiH})_n$ in Table 1 increase with the increase of n values. Those of $(\text{LiH})_\infty$ in Table 2 are larger than for the linear finite chains but are much smaller than the experimental bond length of crystalline LiH (2.045 Å) [25], indicating that the residual anisotropy from one dimensional linear model chain is still affecting the bond length. In Fig. 5, the correlations between

Table 1. Equilibrium properties of the linear, equidistant $(LiH)_n$ for $n = 1\text{-}5$[a]

	LiH	$(LiH)_2$	$(LiH)_3$	$(LiH)_4$	$(LiH)_5$
r_e (Å)	1.615	1.638	1.648	1.653	1.655
$-E$/molecule (a.u.)	7.9647	7.9890	8.0012	8.0083	8.0128
E_{cp}[b] (kcal/mol)	—	12.98	19.92	24.00	26.65
$\Delta_{1\sigma}$[c] (a.u.)	—	0.163616	0.212716	0.234696	0.246710
$\Delta_{2\sigma}$[c] (a.u.)	—	0.148266	0.194218	0.215589	0.227436
q_H[d]	1.5022	1.7160	1.7221	1.7198	1.7186
		1.5271	1.7104	1.7104	1.7079
			1.5201	1.7107	1.7098
				1.5310	1.7101
					1.5321

[a] Using basis set II

[b] Intermolecular stabilization energies per molecule obtained using CP method. a.u. of energy = 627.51 kcal/mol

[c] Bandwidths of splitted molecular orbitals

[d] Mulliken's populations of hydrogen atoms

equilibrium bond lengths and total energies per molecule are presented, and the calculated results of CO method [21] are compared with ours. The results of both methods vary widely along with the number of neighbors explicitly considered and the size of basis sets. The near linear relationship is observed for finite chains. There are some deviations from the relationship in the case of infinite chains. More significant differences can be found between bandwidths of finite chains and those of infinite chains. The bandwidths of finite chains increase with the size of the chains, but those of the infinite chains are very small compared with finite chains. The bandwidths obtained by CO method are 0.00021-0.00034 for 1σ and 0.00475-0.02001 for 2σ [21] which are agreed well with our results. Because the band edges, which are defined by the orbital energies of given type of orbitals, come from the orbitals centered at the boundaries of the clusters, we may conclude that the boundary effect of the model chain is effectively removed by the PL method. The potential curves of the linear $(LiH)_n$'s for $n = 1\text{-}5$ are plotted to compare their relative curvatures in Fig. 6. The larger the size of

Table 2. Equilibrium properties of the linear, equidistant $(LiH)_\infty$

Basis set	I		II	
Model chain[a]	5	7	5	7
r_e (Å)	1.667	1.725	1.708	1.734
$-E$/molecule (a.u.)	8.0479	8.0420	8.0474	8.0422
E_{cp} (kcal/mol)	49.08	46.18	48.90	45.81
$\Delta_{1\sigma}$ (a.u.)	0.00025	0.00020	0.00020	0.00018
$\Delta_{2\sigma}$ (a.u.)	0.02072	0.02230	0.02115	0.02237
q_H	1.6615	1.6650	1.6635	1.6698

[a] The numbers represent n of $(LiH)_n$

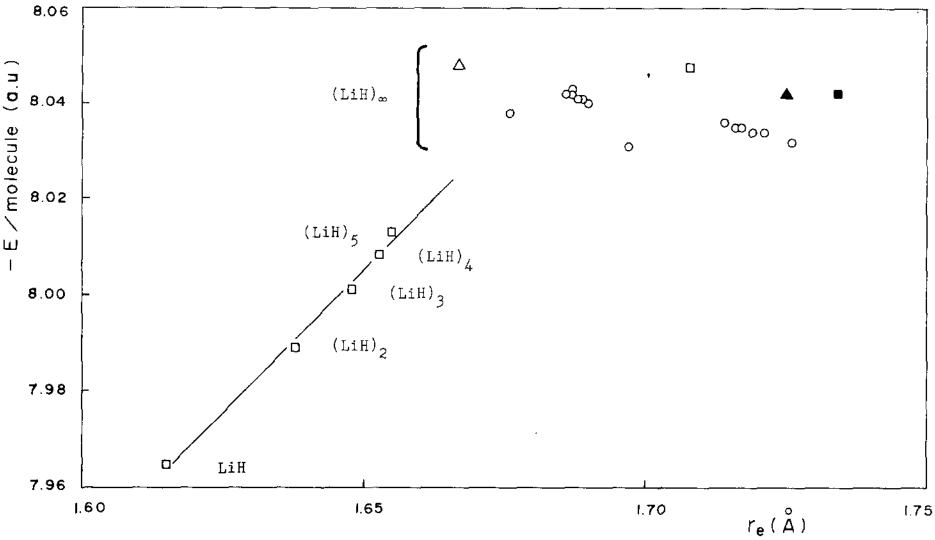

Fig. 5. Correlation between the equilibrium bond lengths and total energies per molecule of the linear, equidistant $(LiH)_n$ for $n = 1$-5 and ∞. △ and ▲: basis set *I*, □ and ■: basis set *I*, △ and □ of $(LiH)_\infty$: $(LiH)_5$ for model chain; ▲ and ■ of $(LiH)_\infty$: (LiH) for model chain; ○: results of the crystal orbital method by varying the number of neighbors and the basis sets (from [21])

the cluster, the larger the curvature of the parabola is. Those of the infinite chains are compared with potential curve of $(LiH)_5$ in Fig. 7. The curvature of the potential curve of $(LiH)_\infty$ using $(LiH)_5$ as a model chain is smaller than the curvature of $(LiH)_5$ chain. The curvature of $(LiH)_\infty$ using $(LiH)_7$ is larger. In order to obtain accurate value of force constant of infinite systems, the intermolecular interactions must be considered at least up to third nearest neighbors as one sees in the case for $(LiH)_7$. The intermolecular stabilization energies of the infinite chains are substantially different from those of the corresponding clusters. From the trend of intermolecular stabilization energies of finite chains, we also conclude that the size of linear, finite chain which have similar value of

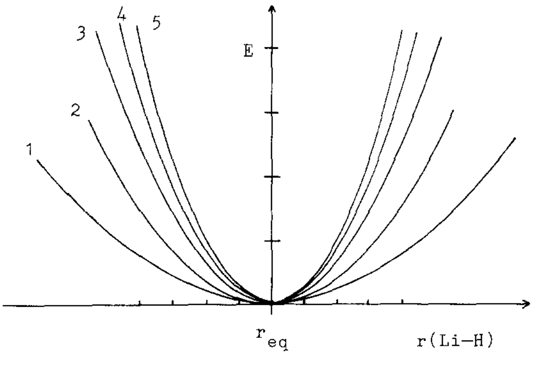

Fig. 6. Comparison of potential curves of the linear, equidistant lithium hydride chains. The numbers in the figure represent *n* of $(LiH)_n$.

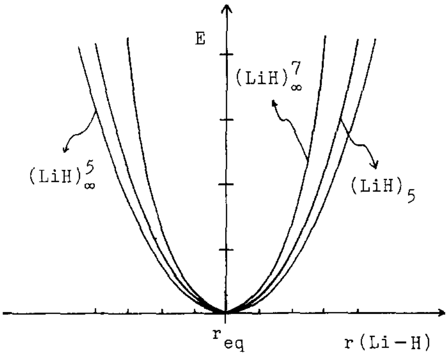

Fig. 7. Comparison of potential curves of $(LiH)_5$ and $(LiH)_\infty$. The superscripts of $(LiH)_\infty$ represent the size of the model chain

intermolecular stabilization energy to $(LiH)_\infty$ is too large to treat by *ab initio* SCF method. The amounts of corrected energies by the CP method are 2.3-3.6 kcal/mole for the finite and infinite chains. The stabilization energies in Table 2 are much larger than hydrogen bond energies and even larger than lithium bond energies. The lithium bond has been studied experimentally and theoretically as an analog of hydrogen bond [28-31]. Addition of one *s* GTF to Li affects only the bond length slightly. We expect that the energetics are much affected by additional polarization functions [32, 33]. The Mulliken's populations of the atoms of LiH are all same for molecules in the all model chain. The present result demonstrates that the modification of the PL method for *ab initio* SCF calculations have been performed successfully for linear chains, and the informations obtained from the PL method are useful in many respects. If the method is properly extended, the PL method is one of successful methods which can be economically applied to the study of solid and possibly to surface studies without losing all the advantages of *ab initio* calculations.

Acknowledgement. This work was supported in part by Korea Research Center for Theoretical Physics and Chemistry and Korea Science and Engineering Foundation.

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