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The Simulated ab Initio Molecular Orbital (SAMO) Method. A Study of the Linear Metallic Hydrogen Chain

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The simulated ab initio molecular orbital (SAMO) crystal orbital method has been used to study an infinite linear equidistant chain of hydrogen atoms. Results obtained using a pattern molecule of 50 hydrogen atoms have been compared with results obtained from truncating this pattern and from the use of smaller non-truncated pattern molecules.

INTRODUCTION

Although the SAMO molecular method has been applied by Day[1] to the study of the highest occupied and lowest unoccupied orbitals of large molecular systems of up to 950 hydrogen atoms simulated from a pattern molecule of 34 hydrogen atoms, and although, where comparison was possible, these calculations were found to agree well with ab initio results, no SAMO crystal orbital study has been reported on a linear infinite chain of hydrogen atoms. The apparent simplicity of this problem is deceptive. Thus it is true that the role played by a chain of hydrogen atoms in the theory of one-dimensional polymers is comparable to that played by the hydrogen molecule in molecular orbital theory, but it is also true that, unlike the hydrogen molecule, the problem of the hydrogen chain is not completely straightforward. Indeed we have chosen this problem for three reasons:

(a) its nature provides the severest possible test of the assumptions of the SAMO crystal orbital method.

(b) it allows us to use large pattern molecules H_n, with n up to 50 hydrogen atoms, close to the limit as $n \rightarrow \infty$.

(c) it allows us to study the effect of pattern molecule truncation on SAMO crystal orbital calculations by systematically truncating H_n, labelling the resulting SAMO calculations $H_{(n,l)}$ where l is the number of single atom cells neighbouring the zero cell, and comparing results with those from non-truncated patterns.

METHOD OF CALCULATION

Since the SAMO method for polymers has been fully described in the literature[2-4] we limit our account here to one of introducing notation and concepts relevant to this paper. As with the ab initio crystal orbital method, the SAMO method for one-dimensional polymers with translational symmetry expands the crystal orbital in terms of Bloch symmetry orbitals

$$\varphi_i(k) = \sum_{\mu} c_{i\mu}(k)\, \Phi_{\mu}(k) \tag{1}$$

Here, the Bloch orbitals are given by

$$\Phi_{\mu}(k) = \sum_{j=-\infty}^{\infty} e^{ikaj}\, \chi_{\mu}^{j} \tag{2}$$

where X_{μ}^{j} is a basis function in the jth translational cell, a is the translational distance and k is a symmetry label restricted to lie in the range

$$-\pi/a < k \leq \pi/a$$

known as the first Brillouin zone.

The complex coefficients $C_{i\mu}(k)$ occuring in equation (1) are given by the solution of the Roothan[5] and Hall[6] eigenvalue equation

$$J(k)\, c(k) = \xi(k)\, c(k)\, \lambda(k) \tag{3}$$

The solutions of equation (3) give, in addition to $C(k)$, $\lambda(k)$ a matrix of real orbital energies which can be plotted against k to give the band structure.

The matrix elements of $J(k)$ and $\xi(k)$ are given by

$$J_{\mu S}(k) = \sum_{j=-N}^{+N} e^{ijka} F_{\mu S}^{j} \tag{4}$$

$$\xi_{\mu S}(k) = \sum_{j=-N}^{+N} e^{ijka} S_{\mu S}^{j} \tag{5}$$

Pattern molecules are used to obtain $F_{\mu\zeta}^{j}$ and $S_{\mu\zeta}^{j}$. These terms are real matrix elements taken over the atomic basis functions in the zero and jth cells

$$F_{\mu\zeta}^{j} = \int \chi_{\mu}^{o}\, F\, \chi_{\zeta}^{j}\, a\tau \tag{6}$$

$$S_{\zeta\mu}^{j} = \int \chi_{\mu}^{\sigma}\, \chi_{\zeta}^{j}\, a\tau \tag{7}$$

In the SAMO crystal orbital method the energy per unit cell, E_{cell}, is evaluated without the calculation of the two electron integrals, from the expression

$$E_{\text{cell}} = \sum_{j=-N}^{+N} \sum_{\mu_j\zeta} D_{\mu\zeta}^{j}\,(\tau_{\mu\zeta}^{j} + V_{\mu\zeta}^{j}) + (a/2\pi) \int_{\substack{\text{Brillonin}\\ \text{zone}}} \sum_{i}^{\text{occ}} \lambda_i(k)\, ak + $$

$$+ {}^{1}\!/_{2} \sum_{j=-N}^{+N} \sum_{A,B} \frac{Z_{A^o} Z_{Bj}}{R_{A^o Bj}} \tag{8}$$

where A^o refers to atom A in the zero cell, B^j to atom B in the jth cell, the prime indicates exclusion of the term where the denominator vanishes and $D_{\mu\zeta}^{j}$, $T_{\mu\zeta}^{j}$, and $V_{\mu\zeta}^{j}$ are given by

$$D_{\mu\zeta}^{j} = a/2\pi \int_{\substack{\text{Brillonin}\\ \text{zone}}} \sum_{i}^{\text{occ}} c_{i\mu}(k)\, c_{i\zeta}(k)\, e^{ijka}\, ak \tag{9}$$

$$T_{\mu\zeta}^{j} = \langle \chi_{\mu}^{o} | -1/2\, \nabla^{2} | \chi_{\zeta}^{j} \rangle \tag{10}$$

$$V_{\mu\zeta}^{j} = \sum_{h=-N}^{+N} \sum_{A}^{\Omega} \langle \chi_{\mu}^{o} | -\frac{Z_{A}}{r_{Ah}} | \chi_{\zeta}^{j} \rangle \tag{11}$$

where Z_A is the charge on atom A, there being Ω atoms in a single unit cell.

RESULTS AND DISCUSSION

In this work the hydrogen atoms are at the near Hartree-Fock equilibrium distance[7] of 1.84 bohr apart and a minimum basis of a single is orbital represented by an STO 4G expansion with coefficient 1.2 is used for each atom. Although we are using a different interatomic distance, our calculations are close to those reported by Karpfen[7] for his STO 4G(c) basis. Since the value of the exponent used in his other basis sets is unclear, comparison with this work is not possible.

By making n even, ab initio calculations were carried out in the closed shell formalism for the pattern molecules H_n. A total of 15 patterns were studied, 13 derived from $n = 6, 8, 10 \ldots 30$ and an additional two from $n = 48$ and $n = 50$. Each H_n pattern molecule allows a SAMO crystal orbital calculation to be carried out on the target system, the linear metallic hydrogen chain, having the same geometry and basis set as the pattern. As shown in Figure 1, the patterns possess an alternating charge density. This feature persists to the center of even the largest pattern molecule. The presence of this alternating charge leads to ambiguity of choice (Figure 2) of some elements occuring in equations (4) and (5).

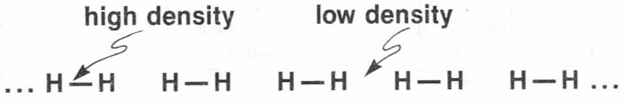

Fig 1. Representation of alteration of charge density in the pattern molecules used to stimulate an infinite linear hydrogen chain.

Although this has little effect on equation (5) where $S_{\mu\xi}^{j}$ terms rapidly converge and are zero beyond the eighth neighbouring cell, its has a significant effect on equation (4). As shown in Table I, with the exception of F^1 which is greater than F^o, the early short range terms decrease in magnitude, longer range terms become positive and the series settles down to one of oscillating pairs of Fock elements which have not completely converged even for a pattern molecule of 50 hydrogen atoms. The choice of »even« Fock

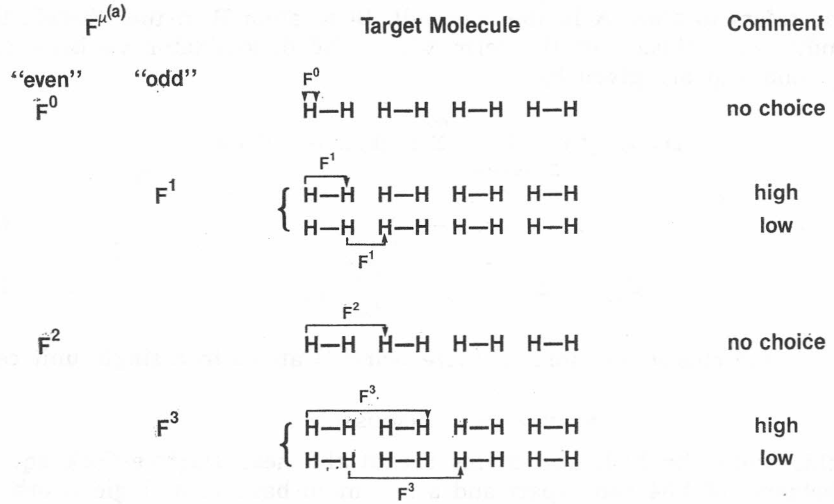

Fig 2. Choice of fock matrix elements for an infinite lineary hydrogen chain having one atom per unit cell.

(a) $F^{\mu} = <\chi^0|\hat{F}|\chi^{\mu}>$, where χ^0 is the 1s orbital in the zero cell and χ^{μ} the 1s orbital in the μth cell.

TABLE I

Fock Matrix Elements for $H_{(8,7)}$, $H_{(50,7)}$ and $H_{(50,49)}$ Calculations

Fock Element	Pattern Molecule		
	$H_{(8,7)}$	$H_{(50,7)}$	$H_{(50,49)}$
F^0	—0.4147394	—0.4097908	—0.4097908
F^1	—0.5003965	—0.4879597	—0.4879597
F^2	—0.1792384	—0.1778965	—0.1778965
F^3	—0.0197508	—0.0219470	—0.0219470
F^4	—0.0016532	—0.0017297	—0.0017297
F^5	—0.0085228	—0.0066821	—0.0066821
F^6	—0.0016525	—0.0013910	—0.0013910
F^7	+0.0046217	+0.0032095	+0.0032095
F^8			+0.0005661
F^9			—0.0019178
F^{10}			—0.0002880
F^{11}			+0.0012283
F^{12}			+0.0001624
.			.
.			.
.			.
F^{43}			+0.0000152
F^{44}			+0.0000015
F^{45}			—0.0000121
F^{46}			—0.0000012
F^{47}			+0.0000107
F^{48}			+0.0000010
F^{49}			—0.0000094

elements is fixed, (Figure 2), F^0 being formed by taking hydrogen with itself and F^2, F^4 etc., always include a low charge density. However, the »odd« Fock elements can be selected to include either a greater preponderance of high or low density terms. The presence of this alternating charge density allows us to divide the pattern molecules H_n into two classes. Where $n = 2m$ and m is even the charge between the central hydrogens will be of low density; for example, hydrogens 4 and 5 in H_8. Where $n = 2m$ and m is odd, the charge between the central hydrogens will be of high density; for example, hydrogen 25 and 26 in H_{50}. Since in the SAMO crystal orbital method the initial Fock element is transfered from as central a position as possible in the pattern molecule, the size of the pattern will determine whether one choses the »odd« Fock elements to be low or high. From Table II, where we compare the elements transfered from H_{50}, we see that the low density choice »odd« Fock elements are much smaller in magnitude and that they converge faster than those from the high density choice. Clearly the pattern molecules used to simulate systems like metallic hydrogen are chemically not like the target system. This is why metallic hydrogen provides us with a severe test of the SAMO crystal orbital method, a test we have made even more stringent by comparing H_8, a pattern of low density central charge, with H_{50}, one of high density central charge. The pattern H_8 was also chosen because it is about the largest size pattern molecule one would want to use in SAMO work.

TABLE II

Fock Matrix Elements Taken from $H_{(50,49)}$ with low and high Density Choice

Fock Element	Low Density	High density(a)
F^0	—0.4097908	
F^1	—0.4512327	—0.4879597
F^2	—0.1778965	
F^3	—0.0324169	—0.02197470
F^4	—0.0017297	
F^5	—0.0020727	—0.0066821
F^6	—0.0013910	
F^7	+0.0006674	+0.0032095
•	•	•
•	•	•
•	•	•
F^{43}	+0.0000001	+0.0000152
F^{44}	+0.0000015	
F^{45}	+0.0	+0.0000121
F^{46}	—0.0000012	
F^{47}	—0.0	—0.0000107
F^{48}	+0.0000010	
F^{49}	—0.0	—0.0000094

(a) No entry appears where the high density Fock element has the same value as the low density element.

The single half filled band derived from a linear infinite chain of hydrogen atoms having a single is orbital per unit cell, was sampled over the range $k = 0$ to $k = \pi/a$ at 41 points; the filled half band ($k = 0$ to $k = \pi/2a$)

being sampled by the first to the twenty first k point. For a regular chain of atoms distance a apart, we can, from equations (6) and (7) define

$$F^{\mu} = \langle \chi^{o} \mid \hat{F} \mid \chi^{\mu} \rangle \tag{12}$$

$$S^{\mu} = \langle \chi^{o} \mid \chi^{\mu} \rangle \tag{13}$$

$$S^{o} = 1 \tag{14}$$

where χ^{o} and χ^{μ} are the basis functions in the zero and μth cells respectively. The energy of the single band, as a function of k, is then given by

$$E(k) = \frac{F + 2 \sum_{\mu=1}^{1} \cos(\mu a k) F^{\mu}}{1 + 2 \sum_{\mu=1}^{\Omega} \cos(\mu a k) S^{\mu}} \tag{15}$$

where the calculation has been performed in the 1 th neighbour approximation.

We have evaluated the root mean square error between the energy bands produced from the result $H_{(50,49)}$ using the pattern molecule H_{50} and those from:

(a) the truncation of H_{50}, that is $H_{n,1}$ $(n = 50 \; 1 < 49)$

(b) ab initio calculations on smaller pattern molecules, not truncated, that is $H_{(n,n-1)}$ $(n < 50)$

This error analysis was carried out for each k point over the filled half band and for each k point over the full band using the expression

$$\left\{ \frac{\sum_{i=1}^{M} [E(k_i) - E'(k_i)]}{M} \right\}^{1/2} \tag{16}$$

where $M = 21$ filled half band only
$M = 41$ full band

and $E'(k)$ is the energy at point k of the reference calculation $H_{(50,49)}$

The errors increase smoothly with truncation. In Table III we sample the energies of the occupied half band obtained from calculations $H_{(8,7)}$, $H_{(50,7)}$,

TABLE III

Single half Filled Band Energies for Metallic Hydrogen from Stimulated Calculations $H_{(8,7)}$, $H_{(50,7)}$ and $H_{(50,49)}$

k	$H_{(8,7)}$	$H_{(50,7)}$	$H_{(50,49)}$
0	—0.755973	—0.743832	—0.744498
π/4a	—0.728434	—0.715304	—0.714521
π/2a	—0.630499	—0.618047	—0.619355
3π/4a	—0.460098	—0.441430	—0.438497
π/a	—0.078079	—0.075872	—0.072141
RMS error	0.013660	0.003468	0.0

and $H_{(50,49)}$ and give the root mean square error in the bands from $H_{(8,7)}$ and $H_{(50,7)}$ when compared with the result from $H_{(50,49)}$. This shows the effect on band structure of long range terms; terms that can be computed from a multipole expansion[8,9]. Consideration of equation (15) shows that at $k = \pi/a$ only »even« Fock elements contribute to the energy. Hence the Fermi surface is unaffected by the ambiguity of choice of »odd« Fock elements. However, this choice makes a significant difference at the bottom of the band where both »even« and »odd« Fock matrix elements contribute with equal weighting and the high density choice lowers the energy. Metallic hydrogen energy calculations, where the unit cell contains one hydrogen atom, cell (1), do not agree with those where the unit cell contains two hydrogen atoms, cell (2). Thus, considering the simplest case of a chain of four hydrogen atoms $H_{(4,3)}$, for cell (1) the energies at the ends of the single band ($k = 0$ and $k = \pi/a$) are, from equation (15)

$$E_{\text{cell}(1)}\,(o, \pi/2) = \frac{F^o \pm 2F^1 + 2F^2 \pm 2F^3}{1 \pm 2S^1 + 2S^2 \pm 2S^3} \tag{17}$$

In the case of cell (2), the resulting two bands, a lower valence and an upper conduction band, are degenerate at $k = \pi/2a$ and have the energy at $k = 0$ for the valence band immediately below that of $k = \pi/a$ for the conduction band. Thus, the lowest energy of the valence band and the highest energy of the conduction band is given by the solution of the 2×2 determinant

$$\begin{vmatrix} J_{11} - \xi_{11} E & J_{12} - \xi_{12} E \\ J_{21} - \xi_{21} E & J_{22} - \xi_{22} E \end{vmatrix} = 0$$

which for $k = 0$ is

$$E_{\text{cell}(2)} = \frac{F^o \pm 2F^1 + 2F^2 \pm 2F^3}{1 \pm 2S^1 + 2S^2 \pm S^3} \tag{18}$$

Cell (2) results can therefore be simulated in a cell (1) calculation if F^μ and S^μ are given a weight of 1 rather than 2, when $\mu = l$. In Table IV we give the energy per unit cell obtained from cell (1) calculations. The errors in energy are relatively small and, unlike the SAMO molecular case where errors in total energy are random, in the SAMO crystal orbital case they increase smoothly with truncation. Thus, even when $H_{(50,49)}$ is truncated to $H_{(50,17)}$ the energy difference is only of the order of 0.5 millihartree.

TABLE IV

Energies per Unit Cell Determined from Calculations $H_{(50,49)}$, $H_{(50,7)}$ *and* $H_{(8,7)}$

Calculation	Energy Energy	Difference $\Delta E \times 10^7$
$H_{(50,49)}$	—0.5343152	0
$H_{(50,7)}$	—0.5337966	+5186
$H_{(8,7)}$	—0.5406679	—63527

CONCLUSION

We have tested the SAMO crystal orbital method by deliberately choosing to study a system that presents a problem not present in our previous studies of saturated systems. Where the problem of ambiguity of choice in the Fock matrix element arises we have chosen to transfer elements from the worst situation. Our study shows that, although even under these conditions, the SAMO crystal orbital method is able to get the »broad picture« correct, errors arise due to the neglect of significant terms in the slowly decaying long range Fock elements and to changes that occur in short range terms taken from small pattern molecules. Indeed, the effect of truncating pattern size is more damaging than the effect of truncating the number of cells from a given pattern. Although future SAMO crystal orbital calculations should be performed with large pattern molecules these should not be much larger than those used in the past. Work on the inclusion of the long range terms through the use of a multipole expansion technique is currently in hand.

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SAŽETAK

Simulirana ab initio molekularno-orbitalna (SAMO) metoda

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Upotrijebljena je simulirana ab initio molekularno-orbitalna (SAMO) metoda za studiranje beskonačnog linearnog lanca s jednako udaljenim atomima vodika.

Uspoređeni su rezultati dobiveni za modelnu molekulu od 50 atoma vodika s rezultatima dobivenim reduciranjem tog modela i za manje ne-reducirane modelne molekule.