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Molecular geometries from spin Hamiltonian calculations through simultaneous optimization of geometry and wave function

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The recently developed spin Hamiltonian approach to conjugated π-electron molecules is reexamined. A simultaneous optimization of the geometry and wave functions, achieved by the use of the conjugate gradient method, facilitates calculations of the molecular geometries in the ground and excited electronic states. The computation time increases approximately *linearly* with the number of basis functions, making calculations for molecules having up to 18 carbon atoms (48 620 basis functions) readily available. Geometries of several benzenoid hydrocarbons are optimized and the results are discussed.

Key words: Spin Hamiltonian — Optimization of geometry — Conjugated molecules

1. Introduction

The reputation of the molecular orbitals (MO) methods in predicting the structure of stable, non-radical molecules in their ground states is almost as good as it is bad in calculations on radicals, transient species and molecules in excited states. Since the vast part of chemistry (and organic chemistry in particular) concerns with chemical reactions that involve unstable intermediates and transition states (in chemical processes), and excited electronic states (in photochemical reactions), there is an understandable need for quantum-mechanical methods that

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can accurately describe these species. The obvious choice is to invoke the configuration interaction schemes or many-body perturbation theory. They can provide the required description of electronic structure, but at the expense of an enormous use of computational time and the form of wave function that eludes simple interpretation based on the "chemical sense".

Quite recently, a new *ab initio* method that includes electron correlation, based on the spin Hamiltonian has been applied to conjugated organic molecules [1, 2]. For metallic crystals the bulk properties have been reproduced successfully [3]. There is, however, one problem that hinders wide utilization of the spin Hamiltonians in molecular calculations. For molecules with N atoms, one has $\binom{N}{[N/2]}$ basis functions. This rules out computational feasibility of the spin Hamiltonian calculations for N larger than about 10 when traditional methods, involving diagonalization of the Hamiltonain matrix, are used.

For simple spin calculations, based on topological Hamiltonian (which would correspond to the Hückel method in MO theory) there is a remedy for this computational problem [4, 5]. For the *ab initio* approach, Sanchez-Marin et al. [6] have proposed recently a variant of the many-body perturbation theory to approximate the ground state energy. However, this approach seems to suffer from several drawbacks. In particular, selection of the reference states cannot be done automatically. The molecular geometry appears to depend to some extent on the choice of the reference states. The authors claim that using their method they can study (approximately) the electronic structure of molecules up to 20 atoms, but they were able to optimize the geometry of molecules having at most 12 atoms.

The goals of the present paper are twofold. First, we present a computational algorithm that offers the possibility of extremely fast spin Hamiltonian calculations. Second, we employ this algorithm to optimize the geometry of several conjugated hydrocarbons having up to 18 carbon atoms. Even for such large molecules the computations do not require excessive CPU time. In particular, optimization of the [18]-annulene molecule takes only one hour of CPU time on a VAX 780 digital computer.

2. Computational algorithm

Let the molecule under consideration be described by the set of linked pairs of carbon atoms $\{i\text{-}j\}$. The energy to be optimized reads:

$$E[\psi, \{r_{ij}\}] = \sum_{i-j} [R(r_{ij}) - 2g(r_{ij})\langle\psi|\mathcal{P}_{ij}|\psi\rangle / \langle\psi|\psi\rangle], \qquad (1)$$

where r_{ij} is the length of the bond between atoms i and j, R and g are functions of r_{ij} described in [1]. They are extracted from a high-quality *ab initio* calculations on the S_0 and T_1 electronic states of the ethylene molecule. $\mathcal{P}_{ij}$ is the spin bond order operator for the bond $i\text{-}j$. The wave function ψ is a linear combination of the neutral VB determinants built up from the p_z orbitals of the carbon atoms that constitute the molecule. Thus the spin Hamiltonian method is a simplified variant of the VB approach. The reader is referred to [1-3] for more details. From Eq. (1) we see that the energy is a functional of both the trial wave function, ψ, and the set of bond lengths, $\{r_{ij}\}$.

There are several ways to carry out the optimization of E. The traditional approach is to guess some trial geometry and then minimize E with respect to ψ. This yields the energy for the guessed geometry. Repeating this for several sets of $\{r_{ij}\}$ results in optimized bond lengths and the corresponding energy. Optimization of the trial wave function can be achieved by diagonalization of the Hamiltonian matrix associated with the functional (1) or by invoking pseudodiagonalization procedures that are widely employed in "direct CI" calculations [7]. Diagonalization of the Hamiltonian matrix is certainly a great waste of time, since we need the wave function and the corresponding energy of only one electronic state. One has to point out, however, that even a pseudodiagonalization technique used in connection with the geometry optimization is far from being optimal. One has to calculate a quite accurate wave function which will change anyway when $\{r_{ij}\}$ is altered in the next cycle of the geometry optimization. What is really desirable is to optimize the wave function and geometry simultaneously. Unfortunately, such algorithms are lacking in the chemical literature. Therefore, we describe here this kind of computational procedure.

The vector of the first derivatives of E with respect to $\{r_{ij}\}$ (the "geometry gradient") is easily computed from Eq. (1):

$$\gamma_{ij}=\frac{\partial E}{\partial r_{ij}}=R'(r_{ij})-2g'(r_{ij})\langle\psi|\mathcal{P}_{ij}|\psi\rangle/\langle\psi\,|\,\psi\rangle. \tag{2}$$

To optimize the wave function we need a functional derivative of E with respect to $\langle\psi|$ ("the wave function gradient") [8]:

$$|\gamma\rangle=\frac{\partial E}{\partial\langle\psi|}=-2\sum_{i-j}g(r_{ij})(\mathcal{P}_{ij}-\langle\psi|\mathcal{P}_{ij}|\psi\rangle\mathbf{1})\,|\psi\rangle, \qquad \langle\psi\,|\,\psi\rangle=1. \tag{3}$$

Since $|\psi\rangle$ is a linear combination of the basis functions, both $|\psi\rangle$ and $|\gamma\rangle$ are represented by vectors. This means in practice that $\{\gamma_{ij}\}$ and $|\gamma\rangle$ can be combined into one vector, $\boldsymbol{\gamma}$. Similarly, $\{r_{ij}\}$ and $|\psi\rangle$ can be combined into one vector, $\boldsymbol{x}$, which is varied until the minimum of E is found.

Several methods of optimization are known [9]. We cannot use any Newton or pseudo-Newton (variable metric) optimization procedures, since it would require calculation and storage of a matrix of at least $N_b\times N_b$ elements where N_b is the number of basis functions. Because of that we have to choose between the steepest-descent and the conjugate gradient algorithms. The steepest-descent method performs well in the first iteration [10], but convergence of the subsequent optimization cycles is poor [9, 11]. Therefore we use here the conjugate gradient method of Polak and Ribiere [9]. In this approach a function of several variables, $f(\boldsymbol{x})$, is minimized iteratively. In every cycle, a step vector

$$\boldsymbol{s}_k=\lambda_k\left[\boldsymbol{\gamma}_k+\frac{\boldsymbol{\gamma}_k\cdot(\boldsymbol{\gamma}_k-\boldsymbol{\gamma}_{k-1})}{\boldsymbol{\gamma}_{k-1}\cdot\boldsymbol{\gamma}_{k-1}}(\boldsymbol{s}_{k-1}/\lambda_{k-1})\right] \tag{4}$$

is added to the old vector, x_k. The step size, λ_k, is determined from the condition that the function of the new vector

$$x_{k+1} = x_k + s_k \tag{5}$$

has a minimal value. One can thus say that a minimization of the function of several variables $f(x)$ is replaced by a series of minimizations of functions of one variable, $f_k(s_k)$. Finally, one should note that γ_k and γ_{k-1} are gradients of $f(x)$ for $x = x_k$ and $x = x_{k-1}$, respectively, and the recurrence (4) is initialized with

$$s_1 = \lambda_1 \gamma_1 . \tag{6}$$

In optimization of the functional (1) we in fact use two different step sizes, one for the "wavefunction" and one for the "geometrical" part of x. This brings $E[\psi, \{r_{ij}\}]$ into the series of functions of two variables. The minimum of E with respect to these variables is calculated without any serious computational effort and at the same time the convergence is greatly enhanced.

Summing up, in every cycle, the "wavefunction" gradient is calculated first. This step of optimization takes time proportional to the number of basis functions. Next, the "geometry" gradient is computed. This requires a negligible amount of time. Then, some auxiliary quantities that are used in the two-variable optimization are formed. This again takes a time proportional to N_b. The step vector is calculated from Eq. (4), but with two different λ's (see above). After performing the two-variable optimization, we obtain a new set of bond lengths $\{r_{ij}\}$ and the improved wavefunction, ψ. The procedure is repeated until the norms of both "geometrical" and "wavefunction" gradients drop below some prescribed threshold.

In the following calculations, we imposed a tolerance of 10^{-3} for the gradient norms. This resulted in an error less than 10^{-3} [Å] for the bond lengths and less than 10^{-5} a.u. for the energy.

3. Results

Using the technique developed in the previous section, we optimized molecular geometries of several π-conjugated hydrocabons both in the ground (S_0) and, for some of them, in the first excited triplet electronic (T_1) state. Before presenting the results, we comment on the computational aspects of the calculations.

In Table 1 we show the optimized total energies of some conjugated hydrocarbons together with the respective numbers of carbon atoms (N), numbers of carbon-carbon bonds (M) and numbers of the basis functions. Total number of iterations required to attain the required accuracy (see above paragraph) is also reported together with the CPU time being spent per iteration.

As expected, the CPU time per iteration grows linearly with the number of the basic functions:

$$t \approx 2 \cdot 10^{-5} N M N_b \text{ [s]}. \tag{7}$$

Table 1. Spin Hamiltonian calculations[a]

Molecule	Electronic state	N	M	Number of basis functions	Number of iterations	CPU time per iteration (s)[b]	E_0 [au]
Benzene	S_0	6	6	20	3	1.7	−0.34655
Benzene	T_1	6	6	20	4	1.4	−0.25383
Naphthalene	S_0	10	11	252	10	2.5	−0.58620
Naphthalene	T_1	10	11	252	10	2.5	−0.51698
Biphenylene	S_0	12	13	924	11	4.1	−0.70238
(*E*)-stilbene	S_0	14	15	3 432	13	12.7	−0.81175
(*E*)-stilbene	T_1	14	15	3 432	13	12.7	−0.75115
Anthracene	S_0	14	16	3 432	14	13.7	−0.82392
Phenanthrene	S_0	14	16	3 432	12	14.0	−0.82874
Pyrene	S_0	16	19	12 870	16	71.1	−0.95526
Pyrene	T_1	16	19	12 870	14	71.9	−0.90472
(18)-annulene	S_0	18	18	48 620	13	302.1	−0.98640
Triphenylene	S_0	18	21	48 620	13	360.3	−1.07304
Triphenylene	T_1	18	21	48 620	14	354.9	−1.01633

[a] Planar geometries assumed for all molecules. Tolerance for the gradient norm: 10^{-3}
[b] VAX 11/780 digital computer

This means that even large systems can be treated using moderate-size digital computers.

First, we report results on the ground state geometries of linear polyenes. There are some discrepancies (of the order of ±0.002 [Å]) between our results and the bond length reported by Sanchez-Marin et al. [1] for small (2 to 10 atoms) molecules. These differences are not inherent to our computational procedure since they also persist in a standard full diagonalization/point-by-point optimization. This indicates that the authors of [1] probably used in their calculations a slightly different set of parameters from that quoted in their paper. Nevertheless,

Table 2. Ground state geometries of linear polyenes[a]

Bond	Number of atoms (N)								
	2	4	6	8	10	12	14	16	18
1-2	1.345 (44)	1.352 (51)	1.353 (53)	1.353 (53)	1.353 (53)	1.354 (53)	1.354	1.354	1.353
2-3		1.443 (45)	1.441 (42)	1.440 (41)	1.440 (49)	1.440 (49)	1.439	1.440	1.440
3-4			1.359 (60)	1.362 (62)	1.363 (60)	1.363 (61)	1.363	1.363	1.363
4-5				1.436 (38)	1.435 (38)	1.435 (43)	1.435	1.435	1.435
5-6					1.364 (65)	1.365 (64)	1.365	1.365	1.365
6-7						1.434 (42)	1.434	1.433	1.433
7-8							1.365	1.366	1.366
8-9								1.433	1.433
9-10									1.366

[a] Exact results [2] for $N = 2, 4, 6, 8$ and 10 and approximate results [6] for $N = 12$ (last two digits) quoted in parenthesis

these differences are very small and do not alter general observations that we comment on below.

The most significant feature of the calculated geometries of the ground state of linear polyenes is the occurrence of almost constant bond alternation pattern in the central parts of molecules. The bond lengths of 1.366/1.433 [Å] compare very favorably with the experimental values for (*E*)-polyacetylene [14] (1.36 and 1.44 [Å]). This means that the spin Hamiltonian calculations are capable of incorporating electron correlation effects which are responsible for a proper balance between these bond lengths. For the T_1 state of octadecanonaene a significant soliton structure is predicted to occur (Table 3).

The optimized geometries for several π-conjugated systems are listed in Table 4. Experimental geometries together with those calculated from molecular mechanics [12] are shown for comparison. Some nonplanar molecules, such as biphenyl and (*E*)-stilbene are also included in Table 4, even if their planar geometry can differ significantly from the actual one.

As one can conclude from Table 4, the spin Hamiltonian calculations have their own merits and defects. There is a good reproduction of the patterns of shorter and longer bonds which is, as one should remember, obtained without any empirical parametrization whatsoever. On the other hand, there is some artificial tendency of "equalization" of the bond lengths. In particular, the almost single bonds (like the inter-ring bond in biphenylene) are calculated too short, while the almost double bonds (like the "a" bond in (*E*)-stilbene) are predicted too long. It is not clear at this moment whether this is an inherent defect of the spin Hamiltonian method or results from the fact that the functions R and g (Eq. (1)) were retrieved from the *ab initio* calculations on the ethylene molecules that were carried out within a rather narrow range of carbon-carbon bond lengths. This could result in a rather poor representation of the above functions by the polynomials quoted in [1].

Let us discuss briefly the results for individual molecules. [18]-annulene is a particularly interesting case. There is a disagreement between predictions from various quantum-mechanical calculations [13], but in general SCF methods favor the structure with a pattern of alternating single and double bonds, while CI approaches favor an aromatic structure. The spin Hamiltonian calculations yield perfectly equal bond lengths.

Marked differences can be observed between the geometries of S_0 and T_1 electronic states of (*E*)-stilbene. The central double bond becomes much longer in the triplet state. This, being a sign of a weakened bond strength, facilitates the rotation

Table 3. The T_1 state geometry of octadecanonaene

Bond	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	9-10
Bondlength [Å]	1.362	1.425	1.389	1.399	1.412	1.379	1.428	1.369	1.434

Table 4. Ground state molecular geometries of selected π-conjugated systems[a]

Molecule/bonds		Bond lengths [Å]		
		Exp.	MMPI[b]	Spin Hamiltonian[c]
Benzene		1.399 ± 0.001	1.397	1.394 (1.414)
Naphthalene	a	1.412	1.420	1.408 (1.394)
	b	1.371	1.377	1.381 (1.409)
	c	1.422	1.427	1.413 (1.408)
	d	1.420 ± 0.008	1.412	1.407 (1.427)
Biphenylene	a	1.400	1.397	1.394
	b	1.400	1.397	1.392
	c	1.400	1.403	1.398
	d	1.490	1.491	1.443
(*E*)-stilbene	a	1.338	1.351	1.361 (1.385)
	b	1.473	1.477	1.440 (1.425)
	c	1.406	1.407	1.399 (1.425)
	d	1.393	1.395	1.392 (1.385)
	e	1.393	1.397	1.395 (1.404)
	f	1.391	1.397	1.395 (1.404)
	g	1.390	1.397	1.392 (1.385)
	h	1.402	1.405	1.399 (1.425)
Anthracene	a	1.418	1.430	1.413
	b	1.375	1.369	1.377
	c	1.444	1.439	1.418
	d	1.433	1.424	1.414
	e	1.405 ± 0.008	1.405	1.400
Phenanthrene	a	1.394	1.408	1.403
	b	1.401	1.386	1.386
	c	1.409	1.419	1.406
	d	1.420	1.412	1.404
	e	1.465	1.460	1.426
	f	1.350	1.361	1.373
	g	1.453	1.444	1.422
	h	1.423	1.418	1.407
	i	1.386 ± 0.008	1.383	1.385
Pyrene	a	1.395	1.396	1.393 (1.395)
	b	1.406	1.405	1.401 (1.416)
	c	1.438	1.448	1.423 (1.406)
	d	1.367	1.361	1.372 (1.396)
	e	1.425	1.416	1.410 (1.416)
	f	1.430 ± 0.004	1.433	1.415 (1.412)
[18]-annulene[d]		1.382/1.419	1.397/1.402	1.397
Triphenylene	a	1.397	1.402	1.401 (1.404)
	b	1.381	1.389	1.388 (1.393)
	c	1.410	1.415	1.404 (1.408)
	d	1.413	1.412	1.403 (1.420)
	e	1.458 ± 0.006	1.466	1.431 (1.416)

[a] Bonds designation and experimental geometries from [12] except as indicated otherwise; [b] [12]; [c] Planar geometries assumed for all molecules. In parenthesis geometrical parameters for the T_1 electronic state; [d] MNDOC geometry [13]

around this bond. The $(Z) \rightarrow (E)$ isomerization of stilbene is well known to proceed through the T_1 state. Not surprisingly, upon the excitation the geometry of the benzene rings remains almost unchanged.

4. Conclusion

Geometries of several conjugated hydrocarbons were optimized for the first time within an *ab initio* spin Hamiltonian method. This allowed us to judge the drawbacks and merits of this approach. We conclude that the spin Hamiltonian calculations can be performed in a routine matter even for quite large molecules. The calculations has a chance to become a valuable tool for chemists studying intermediate products and excited states of organic molecules.

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References

1. Said M, Maynau D, Malrieu JP, Garcia-Bach MA (1984) J Am Chem Soc 106:571; Said M, Maynau D, Malrieu JP (1984) J Am Chem Soc 106:580
2. Sanchez-Marin J, Malrieu JP (1985) J Phys Chem 89:978; Sanchez-Marin J, Malrieu JP (1985) J Am Chem Soc 107:1985
3. Malrieu JP, Maynau D, Daudey JP (1984) Phys Rev B30:1817
4. Cioslowski J (1987) Chem Phys Lett 134:507
5. Cioslowski J (1987) MATCH 22:245
6. Sanchez-Marin J, Malrieu JP, Maynau D (1987) Int J Quantum Chem 31:903
7. Davidson ER (1983) Methods in computational molecular physics. In: Diercksen GHF, Wilson S (eds) Reidel, Dordrecht, and the references cited therein
8. Cioslowski J (1987) Int J Quantum Chem 31:451
9. Polak E (1971) Computational methods in optimization. Academic Press, New York, and the references cited therein
10. Cioslowski J (1987) J Chem Phys 86:2105
11. Dagotto E, Moreo A (1985) Phys Rev D31:865
12. Kao J, Allinger NL (1977) J Am Chem Soc 99:975
13 Thiel W (1981) J Am Chem Soc 103:1420 and the references cited therein
14. Yannoni CS, Clarke TC (1983) Phys Rev Lett 51:1191