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Semiempirical Calculations on Triplet and Doublet States

A Comparison between the Restricted Open-Shell SCF and the Limited Configuration Interaction Method*

G. Wagnière

Institute of Physical Chemistry, University of Zürich, Zürich, Switzerland

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Restricted open-shell SCF calculations are carried out on triplet states of π electron systems and doublet states of some of their ions. The results are compared with the ones obtained by limited configuration interaction and by the use of Koopman's theorem. For some examples open-shell SCF wavefunctions are expanded into linear combinations of Slater determinants representing configurations built from closed-shell SCF orbitals. This allows a more detailed comparison of the different methods of calculation.

Berechnungen nach der beschränkten SCF Methode für offene Schalen werden an Triplettzuständen von π-Elektronensystemen und Dublettzuständen einiger ihrer Ionen ausgeführt. Die Resultate werden mit denjenigen verglichen, welche die beschränkte Konfigurationswechselwirkung und der Satz von Koopmans liefern. Die SCF Wellenfunktionen für offene Schalen werden, für gewisse Beispiele, in Linearkombinationen von Slater-Determinanten entwickelt, welche aus SCF Orbitalen für geschlossene Schalen aufgebaut sind und verschiedene Konfigurationen darstellen. Dies erlaubt einen eingehenderen Vergleich der verschiedenen Berechnungsmethoden.

Des calculs selon la méthode SCF avec restriction pour les couches ouvertes sont effectués sur les états triplets de systèmes d'électrons π et sur les états doublets de certains de leurs ions. Les résultats sont comparés à ceux obtenus par la méthode d'intéraction de configurations limitée et par l'emploi du théorème de Koopmans. Pour certains exemples les fonctions SCF à couches ouvertes sont développées en combinaison linéaire de déterminants de Slater représentant des configurations bâties à partir d'orbitales S.C.F. de couches fermées. Cela permet une comparaison plus détaillée des différentes méthodes de calcul.

I. Introduction

The energy and wavefunction of the lowest triplet state of a neutral molecule or the ground state of a radical ion may, in practice, be calculated in different ways.

a) The most fundamental and straightforward method, but perhaps also the most tedious one mathematically, is by configuration interaction. The solution is written as a linear combination of Slater determinants representing different configurations of appropriate symmetry. Even within the usual simplifications the number of excited configurations of a π electron system rapidly becomes immense as the size of the system increases. Therefore, in numerical work only a limited number of configurations is generally taken into account, and it is not always

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trivial to pick out the ones of primary importance. The influence of multiply excited configurations has been systematically explored in only rather few cases [1 – 5].

b) In the restricted open-shell SCF method the wavefunction is written in form of a Slater determinant, or a linear combination thereof, representing the lowest triplet (or doublet) configuration. One starts out with an eigenfunction of the total spin squared, S^2. Under this restriction the one-electron orbitals are then varied to minimize the energy. The method has been formulated by ROOTHAAN in a manner very convenient for LCAO–MO calculations [6].

c) For the sake of completeness — although we will not directly be concerned with it here — we thirdly mention the unrestricted open-shell SCF method. Here every spinorbital may have a different spatial part. The solution is in general not an eigenfunction of S^2. The spatial parts of the α spinorbitals and β spinorbitals are varied separately to minimize the energy [7]. Eigenfunction of S^2 may then be gained by projection operator techniques [8]. As is well known, the method takes into account, to a large extent, the correlation between electrons of unlike spin. In contrast to the restricted open-shell SCF method it is, for instance, possible to predict the occurrence of negative spin densities. We note that the orbitals obtained both by the restricted and unrestricted method transform according to irreducible representations of the symmetry group of the system.

In this paper we compare, within the frame of semiempirical LCAO–MO calculations, results obtained by limited configuration interaction with ones derived from the restricted open-shell SCF method. Approximations, such as the neglect of differential overlap, and semiempirical parameters are in both cases of course always taken to be the same and are to be found in Ref. [9]. This supplements and extends some investigations carried out by HOYLAND and GOODMAN [10 – 13]. These authors studied ionization energies, electron affinities and charge distributions in positive and negative ions of hydrocarbons. They compared data derived from closed-shell SCF calculations and the application of Koopmans' theorem with corresponding results of restricted open-shell SCF calculations. HOYLAND and GOODMAN also calculated lowest triplet energies by the latter method, comparing their results with limited configuration interaction calculations by PARISER [14].

An informative way to carry out such comparisons is to translate the solutions obtained by open-shell SCF methods into the configuration interaction "language". The open-shell orbitals are written in terms of a given set of orthonormal one-electron functions — such as closed-shell SCF orbitals of the ground state — with which configuration interaction calculations have been performed. The open-shell Slater determinants are then expanded, and this expansion may be interpreted as a superposition of various configurations. Such a procedure can, in principle, also be applied to unrestricted open-shell solutions.

II. Triplet States

The nondegenerate ground configuration and the three components of the lowest triplet configuration of a system of $2N$ electrons may be written

$$\Phi_0 = |\,\varphi_1\,\bar{\varphi}_1\cdot\cdots\cdot\varphi_N\,\bar{\varphi}_N\,| \tag{1}$$

$$ {}^3\Phi_N^{N+1} = \begin{cases} |\,\varphi_1'\,\bar{\varphi}_1'\cdot\cdots\cdot\varphi_{N-1}'\,\bar{\varphi}_{N-1}'\,\varphi_N'\,\varphi_{N+1}'\,| & \text{(2a)} \\ \dfrac{1}{\sqrt{2}}\{|\varphi_1'\bar{\varphi}_1'\cdots\varphi_{N-1}'\bar{\varphi}_{N-1}'\varphi_N'\bar{\varphi}_{N+1}'| - |\varphi_1'\bar{\varphi}_1'\cdots\varphi_{N-1}'\bar{\varphi}_{N-1}'\varphi_{N+1}'\bar{\varphi}_N'|\} & \text{(2b)} \\ |\,\varphi_1'\,\bar{\varphi}_1'\cdot\cdots\cdot\varphi_{N-1}'\,\bar{\varphi}_{N-1}'\,\bar{\varphi}_N'\,\bar{\varphi}_{N+1}'\,|\,. & \text{(2c)} \end{cases} $$

If the one-electron functions φ_i are chosen to minimize the energy of the ground configuration, subject to the usual orthonormality constraints, we call them closed-shell SCF orbitals. If, on the other hand, they are calculated to minimize the energy of the lowest triplet configuration we name them restricted open-shell SCF orbitals and designate them by φ_i'. In the first case we have the usual Hartree-Fock approximation $\Phi_0 \approx \Psi_0$, in the second case we assume ${}^3\Phi_N^{N+1}$ to approximate ${}^3\Psi_1$; Ψ_0 and ${}^3\Psi_1$ being the exact wavefunctions for the ground and lowest triplet state.

Suppose we know both the φ_i and φ_i' for an actual system in an appropriate LCAO form. We may write the φ_i' in terms of the "complete" orthonormal set:

$$\varphi_i' = \sum_j a_{ij}\,\varphi_j$$

and introduce these expressions into any of the Slater determinants (2a, b, c). These determinants are then expanded into linear combinations of configurational functions built from the φ_j. In general, in the absence of symmetry, the number of terms in such an expansion is of the order of $(2N)^{2N}$. However, in many cases some dominant terms may easily be picked out and are, in themselves, of interest. We will now consider some examples:

1. Butadiene: The orbitals φ_i and φ_i' of butadiene are listed in Table 1. The open-shell orbitals are calculated according to the Roothaan method. In Table 2

Table 1. *Ground and lowest triplet state* SCF *orbitals of butadiene. Pariser-Parr resonance integrals are set equal to* −2.46 eV. *Other parameters are also indicated in* Ref. [9]

	χ_1	χ_2	χ_3	χ_4
φ_1	0.40281	0.58116	0.58116	0.40281
φ_2	−0.58116	−0.40281	0.40281	0.58116
φ_3	−0.58116	0.40281	0.40281	−0.58116
φ_4	−0.40281	0.58116	−0.58116	0.40281

	χ_1	χ_2	χ_3	χ_4
φ_1'	0.28649	0.64647	0.64647	0.28649
φ_2'	−0.64647	−0.28649	0.28649	0.64647
φ_3'	−0.64647	0.28649	0.28649	−0.64647
φ_4'	−0.28649	0.64647	−0.64647	0.28649

	φ_1	φ_2	φ_3	φ_4
φ_1'	0.98220		0.18782	
φ_2'		0.98220		0.18782
φ_3'	−0.18782		0.98220	
φ_4'		−0.18782		0.98220

Table 2. *The wavefunction of the lowest triplet state of butadiene in terms of configurational functions built from closed-shell* SCF *orbitals*

	Φ_2^3	Φ_1^4	Φ_{22}^{34}	Φ_{11}^{34}	Φ_{12}^{33}	Φ_{12}^{44}	Φ_{122}^{334}	Φ_{112}^{344}	E
(I)	0.9487	−0.2162	−0.1377	0.0307	0.1377	−0.0307	−0.0926	−0.0693	1.709
(II)	0.9692	−0.2461							2.085
(III)	0.9673		−0.1720		0.1720		−0.0715		2.066
(IV)	0.9647		−0.1845		0.1845		−0.0353		2.084

(I) "Complete" configuration interaction;
(II) Interaction of singly excited configurations only;
(III) Solution obtained by diagonalizing the matrix of the configurations occurring in the expansion of the open-shell SCF solution;
(IV) Expansion of the open-shell SCF solution. E denotes the energy with respect to the SCF ground state in eV.

the wavefunction of the lowest triplet state is expressed in terms of configurational functions built from closed-shell ground state SCF orbitals. For instance, Φ_{12}^{33} designates a triplet configuration in which one electron has been excited from the filled ground state orbital 1 to the empty orbital 3, another electron from the orbital 2 to the orbital 3:

$$\Phi_{12}^{33} = \frac{1}{\sqrt{2}} \{ | \varphi_1 \bar{\varphi}_2 \varphi_3 \bar{\varphi}_3 | - | \varphi_2 \bar{\varphi}_1 \varphi_3 \bar{\varphi}_3 | \} .$$

In case I) the matrix of all configurations interacting with Φ_2^3 by symmetry is diagonalized. We note that the energy obtained is significantly lower than in any of the other, more approximate, methods. In case II) only singly excited configurations are considered, an approximation which is very frequently adopted, especially for larger systems. In case VI) the open-shell solution is expanded as described above. We note that the configuration Φ_1^4 is here completely absent. Consequently, the agreement between the energies obtained here and in case II must be viewed as a coincidence. However, all other configurations which in case I) make significant contributions appear also in the expansion of the open-shell solution. If the submatrix of these configurations is diagonalized exactly, one obtains the result given under III).

2. Higher linear polyenes: We notice that the lowest doubly excited configurations with respect to the ground state, Φ_{22}^{34} and Φ_{12}^{33}, play an important role in the expansion of the open-shell SCF solution of butadiene. These configurations are singly excited with respect to Φ_2^3. Table 3 shows an analogous situation for hexatriene. By introducing "bond alternation", i.e. by making the Pariser-Parr resonance integrals unequal for "short" and "long" bonds (changes in electron repulsion integrals were, for simplicity, neglected) the relative contributions of the configurations Φ_{33}^{45} and Φ_{23}^{44} appear to decrease. This is to be expected, due to the increase in the energy gap between bonding and antibonding ground state SCF orbitals. In Table 4 we compare triplet state energies calculated by the open-shell SCF method on one hand and by interaction of all singly excited configurations with respect to the ground state on the other. In general, the differences between results obtained by the two methods are significantly larger when there is "bond alternation" than when all resonance integrals are the same. These differences

Table 3. *The coefficients of the doubly excited configurations in the open-shell expansion of butadiene. A comparison with the coefficients for the corresponding configurations in hexatriene. In the calculations listed under* a) *all Pariser-Parr resonance integrals have been set equal to* −2.46 eV. *In the calculations listed under* b) *the values of the resonance integrals of the "short" bonds were set equal to* −2.63 eV, *of the "long" bonds equal to* −2.01 eV. *All other parameters were chosen as in* Ref. [9]

Butadiene	a) $0.9647\,\Phi_2^3 - 0.1845\,\Phi_{22}^{34} + 0.1845\,\Phi_{12}^{33} + \ldots.$ b) $0.9690\,\Phi_3^2 - 0.1733\,\Phi_{22}^{34} + 0.1733\,\Phi_{12}^{33} + \ldots.$
Hexatriene	a) $0.9428\,\Phi_3^4 - 0.2134\,\Phi_{33}^{45} - 0.2134\,\Phi_{23}^{44} + \ldots.$ b) $0.9571\,\Phi_3^4 - 0.1178\,\Phi_{33}^{45} - 0.1178\,\Phi_{23}^{44} + \ldots.$

seem to increase for very long polyenes in the first case and to decrease in the second case. The number of polyenes investigated here is certainly insufficient to extrapolate this trend to infinity, however.

3. Cyclic polyenes: As was already noted by Hoyland and Goodman, the lowest triplet energy of benzene should, because of symmetry, be the same whether it is calculated by the open-shell method or from closed-shell ground state orbitals by interaction of the four lowest degenerate singly excited configurations. The open-shell orbitals, having to transform according to irreducible representations of the symmetry group D_{6h}, may only be written in terms of closed-shell orbitals belonging to the same irreducible representation. Every representation occurs only

Table 4. *A comparison of lowest triplet excitation energies in* eV *calculated by the open-shell* SCF *method, and by interaction of all singly excited configurations* (C.I.) *with respect to the ground configuration. In the calculations listed under* b) *all Pariser-Parr resonance integrals have been set equal to* −2.46 eV. *In calculations listed under* a) *the values of the resonance integrals of the "short" bonds were* −2.63 eV, *of the "long" bonds* −2.01 eV

Trans-polyenes	Ground state SCF energy	Open-shell SCF method Triplet state SCF energy	 Triplet excitation energy	C.I. method Triplet excitation energy	Difference
Butadiene	a) 79.894	77.810	2.084	2.085	−0.001
exp. 2.6, 3.2[a]	b) 80.257	77.338	2.919	2.742	0.177
Hexatriene	a) 143.198	141.642	1.556	1.511	0.045
exp. 2.0, 2.6[a]	b) 143.548	140.927	2.621	2.327	0.294
Octatetraene	a) 214.447	213.209	1.239	1.193	0.046
	b) 214.773	212.356	2.417	2.113	0.304
Decapentaene	a) 291.652	290.625	1.027	0.997	0.030
	b) 291.948	289.568	2.380	1.989	0.391
Dodecahexaene	a) 373.628	372.736	0.892	0.868	0.024
	b) 373.893	371.567	2.326	1.913	0.413

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[a] Experimental values from Hammond, G. S., and R. S. H. Liu: J. Amer. chem. Soc. **85**, 477 (1963) and from Evans, D. F.: J. chem. Soc. [London] **1960**, 1735. The energy of the 0–0 band is indicated at the left, the energy of the band maximum at the right.

Table 5. *The energy of the lowest triplet state of some benzenoid hydrocarbons. The semiempirical parameters used for these calculations are as indicated in* Ref. [9]

		Open-shell SCF method		C.I. method	
	Ground state SCF energy	Triplet state SCF energy	Triplet excitation energy	Triplet excitation energy	Difference
Naphthalene exp. 2.64[a]	347.098	344.123	2.975	2.627	0.348
Anthracene exp. 1.82[a]	571.668	569.846	1.822	1.737	0.085
Phenanthrene exp. 2.70[b]	578.877	575.859	3.018	2.665	0.353
Pyrene exp. 2.11[b]	725.203	722.970	2.233	2.025	0.208

[a] Lewis, G. N., and M. Kasha: J. Amer. chem. Soc. **66**, 2100 (1944).

[b] Herkstroeter, W. G., A. A. Lamola, and G. S. Hammond: J. Amer. chem. Soc. **86**, 4537 (1964).

once in the set of ground state molecular orbitals: a_{2u}, e_{1g}, e_{2u}, b_{2g}. Bond alternation now reduces the symmetry of benzene to D_{3h} and the same representation occurs twice among the closed-shell orbitals: a_2'', e'', e'', a_2''. Any open-shell orbital may now be written in terms of both bonding and antibonding closed-shell orbitals. The open-shell solution should then also take into account higher singly and multiply excited configurations. An analogous situation is encountered in all polyenes of formal symmetry $D_{(4\nu+2)h}$ upon reduction of this symmetry to $D_{(2\nu+1)h}$ $(\nu = 1, 2, \ldots)$.

4. Polyacenes and related compounds: Triplet state energies of some benzenoid hydrocarbons are shown in Table 5. For naphthalene and phenanthrene rather larger discrepancies appear, of the order of 0.35 eV. We expand the open-shell solution for naphthalene and may write it as

$$0.9804\,\Phi_5^6 + 0.1017\,\Phi_{25}^{66} + 0.1017\,\Phi_{55}^{69} - 0.0919\,\Phi_{35}^{76} + 0.0919\,\Phi_{45}^{86} + \ldots\ldots \qquad (3a)$$

Beyond Φ_5^6 we notice the absence of significant contributions from configurations singly excited with respect to the ground state. Φ_{25}^{66}, Φ_{55}^{69}, Φ_{35}^{76}, Φ_{45}^{86} are all singly excited with respect to Φ_5^6. Other configurations appear to be of secondary importance as the sum of the coefficients squared of (3a) gives 0.9987. The function obtained by interaction of all configurations singly excited with respect to the ground state shows the following dominant terms:

$$0.9266\,\Phi_5^6 + 0.2711\,\Phi_3^8 - 0.1799\,\Phi_4^7 - 0.1634\,\Phi_2^9 - 0.0842\,\Phi_1^{10} + \ldots\ldots \qquad (3b)$$

Expressions (3a) and (3b) clearly demonstrate the very fundamental differences in the two methods, and it is in this sense remarkable that they should give as good an agreement for the energy, using the same set of semiempirical parameters.

5. Systems with heteroatoms: The introduction of a heteroatom into a π electron system may lead to an unsuspected difficulty, as shown in the case of pyridine and aniline (Table 6). The triplet configuration obtained by promoting an electron from the highest filled ground state SCF orbital to the lowest empty one does not

Table 6. *The energy of the lowest triplet state of some compounds containing heteroatoms. In both cases the open-shell procedure does not "reach" the lowest triplet, as obtained by interaction of singly excited configurations*

		Open-shell SCF method		C.I. method	
	Ground state SCF energy	Triplet state SCF energy	Triplet excitation energy	Triplet excitation energy	
Pyridine[a]	165.217	161.112	4.105	4.092	second triplet
				3.779	lowest triplet
Aniline	249.794	246.423	3.371	3.462	second triplet
exp. 3.32[b]				3.107	lowest triplet

[a] The parameters for pyridine are as indicated in Ref. [9], except that $I'_N = 12.00$ eV. $\beta_{CN} = -2.58$ eV.

[b] LEWIS, G. N., and M. KASHA: J. Amer. chem. Soc. **66**, 2100 (1944).

Table 7. *Closed-shell and open-shell triplet orbitals of aniline. Semiempirical parameters are as indicated in* Ref. [9]. *Numbering of atomic orbitals is as shown in Table 12*

	χ_1	χ_2	χ_3	χ_4	χ_5	χ_6	χ_7
φ_1	0.34733	0.55911	0.39846	0.30120	0.39846	0.30120	0.26030
φ_2	0.53418	0.37011	−0.02964	−0.38203	−0.02964	−0.38203	−0.53291
φ_3	0.	0.	−0.51333	−0.48630	0.51333	0.48630	0.
φ_4	0.68881	−0.21518	−0.37173	0.11219	−0.37173	0.11219	0.42152
φ_5	0.	0.	0.48630	−0.51333	−0.48630	0.51333	0.
φ_6	−0.30328	0.57735	−0.22809	−0.29471	−0.22809	−0.29471	0.54490
φ_7	−0.16599	0.41323	−0.38747	0.40482	−0.38747	0.40482	−0.41671

	χ_1	χ_2	χ_3	χ_4	χ_5	χ_6	χ_7
φ'_1	0.50672	0.58359	0.34950	0.23685	0.34950	0.23685	0.21478
φ'_2	0.52808	0.23839	−0.13632	−0.41970	−0.13632	−0.41970	−0.52423
φ'_3	0.	0.	−0.53210	−0.46569	0.53210	0.46569	0.
φ'_4	0.62156	−0.37264	−0.37045	0.16946	−0.37045	0.16946	0.37799
φ'_5	0.	0.	0.46569	−0.53210	−0.46569	0.53210	0.
φ'_6	−0.25891	0.61829	−0.36065	−0.17099	−0.36065	−0.17099	0.48171
φ'_7	−0.10477	0.28535	−0.30323	0.45802	−0.30323	0.45802	−0.55146

	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7
φ'_1	0.97939	0.17052	0.	0.10729	0.	0.00125	−0.01153
φ'_2	−0.18121	0.97844	0.	0.09865	0.	0.00139	−0.00486
φ'_3			0.99921		−0.03941		
φ'_4	−0.08720	−0.11484	0.	0.98108	0.	−0.12857	0.00960
φ'_5			0.03941		0.99921		
φ'_6	−0.00925	−0.01415	0.	0.12142	0.	0.96328	0.23878
φ'_7	0.01386	0.01154	0.	−0.03780	0.	−0.23561	0.97092

tend towards the lowest triplet state upon open-shell minimization. The expansion of the open-shell solution (4a) and the wavefunctions of the lowest triplet states obtained by interaction of nine singly excited* configurations (4b, c) are indicated below for aniline, with corresponding energy values:

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* From orbitals 2, 3, 4 to orbitals 5, 6, 7.

$$0.9798\,\Phi_4^5 - 0.1150\,\Phi_2^5 - 0.0873\,\Phi_1^5 + 0.1254\,\Phi_{44}^{56} - 0.0386\,\Phi_{34}^{55} + \ldots.. \quad (4a)$$

$$E_1' = 3.37\ \mathrm{eV}$$

$$0.9711\,\Phi_4^5 - 0.2192\,\Phi_2^5 - 0.0789\,\Phi_3^6 - 0.0517\,\Phi_3^7 \quad (4b)$$

$$E_2 = 3.46\ \mathrm{eV}$$

$$0.9445\,\Phi_4^6 - 0.2218\,\Phi_3^5 + 0.1803\,\Phi_4^7 + 0.1483\,\Phi_2^7 - 0.0643\,\Phi_2^6 \quad (4c)$$

$$E_1 = 3.11\ \mathrm{eV}$$

The lowest triplet state, as obtained by interaction of singly excited configurations, consists mainly of Φ_4^6. Attempts to minimize the energy of this configurations by the open-shell procedure have run into technical difficulties*.

III. Doublet States

The same set of semiempirical parameters has been used to obtain the results on doublet states of ions listed in Tables 8 to 12 as for the calculations on the triplet states of the neutral species.

Table 8. *Open-shell* SCF *orbitals for butadiene monopositive and mononegative ion. Same parameters as for results in Table 1*

	χ_1	χ_2	χ_3	χ_4
φ_1^+	0.35401	0.61210	0.61210	0.35401
φ_2^+	−0.57667	−0.40920	0.40920	0.57667
φ_3^+	−0.61210	0.35401	0.35401	−0.61210
φ_4^+	−0.40920	0.57667	−0.57667	0.40920

	φ_1	φ_2	φ_3	φ_4
φ_1^+	0.99665		0.08164	
φ_2^+		0.99993		−0.01104
φ_3^+	−0.08164		0.99665	
φ_4^+		0.01104		0.99993

	χ_1	χ_2	χ_3	χ_4
φ_1^-	0.40920	0.57667	0.57667	0.40920
φ_2^-	−0.61210	−0.35401	0.35401	0.61210
φ_3^-	−0.57667	0.40920	0.40920	−0.57667
φ_4^-	−0.35401	0.61210	−0.61210	0.35401

	φ_1	φ_2	φ_3	φ_4
φ_1^-	0.99993		−0.01104	
φ_2^-		0.99665		0.08164
φ_3^-	0.01104		0.99993	
φ_4^-		−0.08164		0.99665

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* *Note added in proof*: The lowest triplet state of aniline may be reached by the open-shell procedure if one starts with a set of initial orbitals such that orbital 5 has the same symmetry as φ_6, orbital 6 the same symmetry as φ_5. For the energy one then obtains: 3.097 eV. The author thanks Dr. C. E. KLOPFENSTEIN for obtaining this result.

Table 9. *Ionization potentials of polyenes,* a) *without,* b) *with "bond alternation" (see Table 4)*

		Open-shell SCF method		Koopmans'	
	Ground state SCF energy	Doublet state SCF energy	Ionization energy	Ionization energy	Difference
Butadiene	a) 79.894	71.538	8.356	8.459	−0.103
exp. 9.10[a]	b) 80.257	71.505	8.752	8.859	−0.107
Hexatriene	a) 143.198	135.644	7.554	7.748	−0.194
exp. 8.26[a]	b) 143.548	135.454	8.094	8.294	−0.200
Octatetraene	a) 214.447	207.399	7.048	7.311	−0.263
exp. ≈7.8[a]	b) 214.773	207.067	7.706	7.967	−0.261
Decapentaene	a) 291.652	284.954	6.698	7.017	−0.319
	b) 291.948	284.493	7.455	7.759	−0.304
Dodecahexaene	a) 373.628	367.189	6.439	6.806	−0.367
	b) 373.893	366.606	7.287	7.619	−0.332

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[a] Averaged experimental values from tables of ionization potentials by R. W. Kiser: U.S. Atomic Energy Commission, June 1960.

1. Butadiene: If we expand the open-shell SCF function of the doublet ground state of the monopositive ion of butadiene (see Tables 8 and 9) we find:

$$\begin{aligned} |\,\varphi_1^+\,\bar{\varphi}_1^+\,\varphi_2^+\,| &= 0.9932\,\Phi_G + 0.1150\,\Phi_1^3 - 0.0110\,\Phi_2^4 \\ &\quad - 0.0013\,\Phi_{12}^{34} + 0.0067\,\Phi_{11}^{33} - 0.0001\,\Phi_{112}^{334} \end{aligned} \tag{5a}$$

$$\Phi_G = |\,\varphi_1\,\bar{\varphi}_1\,\varphi_2\,|\,; \qquad \Phi_1^3 = \frac{1}{\sqrt{2}}\{|\,\varphi_1\,\bar{\varphi}_3\,\varphi_2\,| + |\,\varphi_3\,\bar{\varphi}_1\,\varphi_2\,|\,; \qquad \text{etc.}$$

We compare this expression with the solution obtained by a limited configuration interaction calculation:

$$0.9912\,\Phi_G + 1136\,\Phi_1^3 - 0.0161\,\Phi_2^4 + 0.0497\,\Phi_{12}^{34} - 0.0417_{11}^{34}\,\Phi + 0.0099\,\Phi_{112}^{334}\,. \tag{5b}$$

While there is qualitative agreement for the coefficients of configurations singly excited with respect to the ground state, some discrepancies in relative magnitude and sign appear for the higher configurations. The ionization energy obtained by configuration interaction is 8.294 eV, as compared to 8.356 eV by open-shell minimization and 8.459 eV from Koopmans' theorem.

The pairing properties of alternant hydrocarbons, the complementarity of electrons and holes, is well illustrated if we expand the open-shell solution of the mononegative ion:

$$\begin{aligned} |\,\varphi_1^-\,\bar{\varphi}_1^-\,\varphi_2^-\,\bar{\varphi}_2^-\,\varphi_3^-\,| &= 0.9932\,\Phi_G + 0.1150\,\Phi_2^4 - 0.0110\,\Phi_1^3 \\ &\quad - 0.0013\,\Phi_{12}^{34} + 0.0067\,\Phi_{22}^{44} - 0.0001\,\Phi_{122}^{344} \end{aligned}$$

$$\Phi_G = |\,\varphi_1\,\bar{\varphi}_1\,\varphi_2\,\bar{\varphi}_2\,\varphi_3\,|\,; \qquad \Phi_2^4 = \frac{1}{\sqrt{2}}\{|\,\varphi_1\,\bar{\varphi}_1\,\varphi_2\,\bar{\varphi}_4\,\varphi_3\,| + |\,\varphi_1\,\bar{\varphi}_1\,\varphi_4\,\bar{\varphi}_2\,\varphi_3\,|\}; \qquad \text{etc.}$$

and compare it with (5a).

2. Polyenes, polyacenes and other hydrocarbons: As is to be expected, ionization potentials predicted by Koopmans' theorem are greater than the ones calculated by the open-shell method.

Table 10. *Ionization potentials of some benzenoid hydrocarbons*

	Ground state SCF energy	Open-shell SCF method: Doublet state SCF energy	Open-shell SCF method: Ionization energy	Koopmans' Ionization energy	Difference
Naphthalene exp. 8.5[a]	347.098	339.048	8.050	8.152	−0.102
Anthracene exp. 7.6[a], 8.4[b]	571.668	564.438	7.230	7.402	−0.171
Phenanthrene exp. 7.8[a], 8.6[b]	578.877	571.041	7.836	8.032	−0.196
Pyrene	725.203	717.958	7.245	7.368	−0.123

[a] Averaged experimental values; see Table 9.

[b] See also Wacks, M. E., and V. H. Dibeler: J. chem. Physics **31**, 1557 (1959).

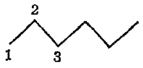
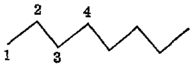
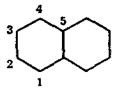
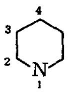
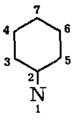
In polyenes the difference increases with growing chain length and appears to be rather insensitive to "bond alternation", in contrast to the triplet states of the neutral molecules. The higher configurations which make important contributions to the expansion of the open-shell solution must, in their energy, be relatively insensitive to changes in resonance integrals for "short" and "long" bonds (for instance, in the case of the configuration Φ_1^3 of the carbonium ion of butadiene the energy of φ_2 is pushed down, the energy of φ_3 is pushed up, leaving the energy of the configuration relatively unaffected). Hoyland and Goodman find much greater differences (of the order of 2 eV) between ionization potentials predicted by Koopmans' theorem and by the open-shell procedure [11]. The discrepancies between the results given here and the ones calculated by these authors may only to a smaller extent be explained by differences in the choice of parameters. We have, in particular, adopted an effective ionization potential for carbon of 9.00 eV, calibrated on spectroscopic data. This, however, should hardly significantly alter the relative values of ionization potentials found by the two methods. As a test we find that charge distributions determined here agree quite well with those calculated by Hoyland and Goodman (see Table 12).

Table 11. *Ionization potentials of some compounds containing heteroatoms*

	Ground state SCF energy	Open-shell SCF method: Doublet state SCF energy	Open-shell SCF method: Ionization energy	Koopmans' Ionization energy	Difference
Pyridine exp. 9.3[a]	165.217	155.838	9.379	9.389	−0.010
Aniline exp. 7.7[a]	249.794	242.948	6.846	7.102	−0.256
Nitrobenzene exp. 10.15[a]	386.034	375.551	10.483	10.606	−0.123

[a] Averaged experimental values; see Table 9.

Table 12. *Charge distributions in monopositive ions. For the polyenes,* a) *means without,* b) *with alternation of resonance integrals*

		from ground state SCF orbitals		from open-shell SCF orbitals
	a)	1. 0.7702	a)	1. 0.6588
		2. 0.9297		2. 1.0188
		3. 0.8001		3. 0.8225
	b)	1. 0.7977	b)	1. 0.6836
		2. 0.9171		2. 1.0236
		3. 0.7851		3. 0.7928
	a)	1. 0.8365	a)	1. 0.7161
		2. 0.9633		2. 1.0457
		3. 0.8197		3. 0.7909
		4. 0.8805		4. 0.9472
	b)	1. 0.8659	b)	1. 0.7504
		2. 0.9551		2. 1.0540
		3. 0.8164		3. 0.7645
		4. 0.8625		4. 0.9311
		1. 0.8195		1. 0.8094
		2. 0.9305		2. 0.9089
		5. 1.0000		5. 1.0633
		1. 1.2275		1. 1.2404
		2. 0.6464		2. 0.6335
		3. 0.7575		3. 0.7595
		4. 0.9648		4. 0.9736
		1. 1.2865		1. 1.2047
		2. 0.9455		2. 1.1187
		3. 0.9845		3. 0.9993
		4. 0.9589		4. 0.9120
		7. 0.8812		7. 0.8540

3. Systems with heteroatoms: Ionization potentials and charge distributions of pyridine and aniline are given in Tables 11 and 12. In pyridine, as in the hydrocarbons, the open-shell method makes charge differences more pronounced. In aniline it has the effect of increasing the positive charge on the nitrogen atom.

IV. Conclusions

Complete configuration interaction calculations being for practical reasons in most cases prohibitive, one has to choose between various more approximate methods to calculate electronic properties, even of π electron systems. We notice that in the case of the energy of triplet states the limited configuration interaction method and the open-shell SCF procedure may lead to results agreeing quite well with each other and with experiment. It is by no means obvious that the same set of semiempirical parameters should give meaningful results with both methods. One may further wonder if for complete configuration interaction calculations these same parameters are really applicable, as shown by the example of butadiene.

Expansion of the open-shell solutions into linear combinations of configurational functions in terms of closed-shell SCF orbitals provides a means of comparing the two methods in detail. It shows how very different the wavefunctions may be and yet lead to similar values for the energy. Other properties may accordingly be predicted quite differently by both methods. Expansion of the open-shell wavefunction can be useful as a means of assessing the importance of certain higher excited configurations and may serve as a starting point for more complete configuration interaction calculations. For doublet states of ions the situation is quite similar. It appears that configuration interaction plays a less important role than for triplet states, and Koopmans' theorem reveals itself to be a useful approximation.

It may certainly be of interest to carry out similar studies with the results of unrestricted open-shell SCF calculations.

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Professor Dr. G. Wagnière
Institut für Physikalische Chemie
der Universität
CH-8001 Zürich