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Linear Combination of Hybrid Orbitals: Acyclic Alkanes*

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A LCHO SCF-CI semiempirical scheme is formulated for compounds of carbon and hydrogen, and far-UV transition energies computed for a number of acyclic alkanes. The type of spectral bands (CH → CH*, etc.) and symmetries of subbands are assigned, and their dependence on conformation and branching discussed. It is argued that, for pentanes and higher alkanes, spectral quantities can be estimated from data on the lower alkanes.

Key words: Hybrids, linear combination of ~ - Saturated organic compounds, MO treatment of ~ - Spectra, far ultraviolet

1. Exposition

Semiempirical SCF-CI calculations of transition energies in organic molecules have mainly been concerned with unsaturated systems, even when "all-valence-electron" basis sets were employed [2]. In the relatively few reports devoted to totally saturated molecules, two main approaches have been taken: in one group of techniques, spectra are computed by one modification or another of the usual "all-valence-electron" constructions, such as "CNDO" and "INDO" [3]; in the other, the basis set comprises the *directed* valence orbitals that emanate from the carbons (e.g. sp^3 in diamond [4]), implemented - when desirable or appropriate - by atomic orbitals on the attached atoms [5, 6]. The latter approach has been termed LCVO or LCHO [Linear Combination of Valence (Hybrid) Orbitals]. It seems that, unlike methods of the first type [7], attempts along the LCHO line have come to a standstill, despite the conceptual advantages of dealing with hybrids [8] and their linear combinations [5a, 9].

One obstacle to the development of LCHO has probably been the simplifying assumption that all bonds at a given carbon are equivalent, e.g. that all C-hybrids in a saturated alkane are pure sp^3. To be fruitful, theory should take into account subtle structural differences and admit general sp^m hybrids (m not necessarily integer [8, 10]). Also, those variants of LCHO that aimed at the calculation of spectra were not made to rely, as heavily as possible, on experience gained in connection with the analogously oriented pi-electron work.

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* "Multi-Conformational Compounds", part X. For part IX, see Ref. [1].

Our starting point has been the definition of a pi-electron scheme in which all integrals were made to depend analytically on structural indices [11]. We then extended the scheme, from a basis of pure $2p$ AO's to a basis of general sp^m hybrids, through application to the carbon skeleton of cyclopropane [12] and cyclobutane [1], two saturated hydrocarbons that have traits in common with unsaturated systems. A further check on the ensuing scheme (still excluding the attached hydrogens) was provided by calculations on the internally rotating cyclopropane-carboxaldehyde [13].

Here we propose to go further: include hydrogens and compute electronic transitions in saturated alkanes. Choice of the necessary formulation (Sect. 2) was followed by parameter-optimization (Appendix). The computed molecular orbitals (Sect. 3) lead to transition energies that mimic experimental features closely enough for assignments. Here we report on some acyclic alkanes (Sect. 4).

Attempts have been described to include Rydberg orbitals in semiempirical calculations of spectra [3a]. We have not done this as yet, but find that one can get quite far with valence orbitals alone, provided enough excited configurations are included in the configuration-interaction (CI) stage. Using, as we do, all virtuals, some configurations are built up that have the requisites for interaction with Rydberg states ("Rydberg/valence-shell conjugates" [14a]). In a way, therefore, the omission of non-valence orbitals can be viewed as such a truncation that is not accompanied by loss of essential species of symmetry and size. Now, parameter-optimization was designed to remedy, as far as possible, the consequences of all approximations - including this truncation - on the computed transition energies. No similar attempts have been made as regards oscillator strengths, and truncation effects here are expected to be more severe.

2. Formulation

For consistency, we computed the molecular geometries by a molecular-mechanical force field [15], rather than take them from experimental sources. Once at hand, they served to construct, at each carbon, four orthogonal hybrids $(1+m)^{-1/2}[(2s)+m^{1/2}(2p)]$, such that [10] $(m_I m_J)^{1/2} = -(\cos T_{IJ})^{-1}$ and $\Sigma(1+m_I)^{-1} = 1$ (T - bond angle; $I, J = 1, 2, 3, 4$). The basis set comprises all carbon hybrids and hydrogen $1s$ AO's. Rotational invariance is automatically guaranteed. Fock matrix elements are formulated as follows (cf. [16]).

2.1 Diagonal

$$F_{ii} = W_i + \sum_{Q \neq I} (Q; \mathrm{ii}) + \tfrac{1}{2} P_{ii}(ii, ii) + \sum_{j \neq i} (P_{jj} - p_j)[(ii, jj) - \tfrac{1}{2}(ij, ji)] + \tfrac{1}{2} \sum_{i' \neq i} P_{ii'}(ii, ii')$$

Here, orbitals i and i' are on atom I, j on J, $\boldsymbol{P}$ is the bond-order-and-charge matrix, p - the occupation number, and $W_i(\mathrm{C}) = (1+m)^{-1}[W_{2s}(\mathrm{C}) + mW_{2p}(\mathrm{C})]$.

Penetration integrals are accounted for (cf. [7]) by a rapidly decreasing function of the distance

$$(Q; ii) \sim Z_Q \exp\left(-a_Q r_{QI}^2\right)$$

where Z_Q is the core charge.

2.2. *Off-Diagonal Bicentric*

$$F_{ij} = \beta_{ij} - P_{ij}(ii, jj) = \beta_{IJ} S_{ij} - P_{ij}(ii, jj)$$

where we followed the practice of making β_{ij} depend on a biatomic factor β_{IJ} and the overlap S_{ij}. Preliminary calculations confirmed [6b] that, in approximate methods of this type, there is no simple relation between β_{IJ} and monoatomic constants β_I and β_J. However, parameter-optimization (Appendix) produced such values of β_{IJ} that could be broken down as $(n_j\beta_I + n_i\beta_J)/2 \max(n_i, n_j)$, where n is the principal quantum number. This expression fits the pi-electron formulation [11] and, incidentally, also oxygen-containing molecules [17]. β_C depends on hybridization through [1] $\beta_C(\mathrm{eV}) = 2.064\,(1 + m)^{-1} - 10.14$.

2.3. *Off-Diagonal Monocentric on Carbon*

$$F_{ii'} = \gamma_{ii'} + \tfrac{1}{2}\{P_{ii}(ii, ii') + P_{i'i'}(ii', i'i') + P_{ii'}\,[3(ii', i'i) - (ii, i'i')]\}$$

where [6b] $\gamma_{ii'} = -[(ii, ii') + (i'i', ii')] + A$. The small term A (<0.1 eV) accounts for the effect of the other two hybrids on C.

It has been our experience that, among the bielectronic integrals that occur in $\boldsymbol{F}$, only those of the forms (ii, ii), $(ii, i'i')$, (ii, jj), (ii, ii') and (ii', ii'), need be conserved [1]. when these are developed as sums over atomic orbitals, we retain [1] and calculate analytically [18] only (ss, ss), (ss, xx), (sx, sx), (xx, xx), (xx, yy), (xy, xy) among the monocentric, and (ss, ss), $(ss, \sigma\sigma)$, $(ss, \pi\pi)$, $(\sigma\sigma, \sigma\sigma)$, $(\sigma\sigma, \pi\pi)$, $(\pi\pi, \pi\pi)$ among the bicentric. Overlap and dipole-length integrals are computed as described [19].

Of the parameters that the scheme requires (Table 1), seven have established values or come from previous work. Others were fixed by optimization (Appendix).

Table 1. Numerical constants

	H ($1s$)	C ($2s, 2p$)
Orbital effective exponent[a]	1.2[b]	3.25[c]
Orbital effective exponent[d]	0.708[e]	1.854[f]
Orbital ionization potential[g] (eV)	−13.605	−21.34 ($2s$) −11.54 ($2p$)
a_Q (A^{-2})	0.1402[e]	0.2456[e]
β_Q (eV)	−10.80[e]	see text

[a] In overlap and dipole-length integrals.

[b] Ref. [20].

[c] Slater value.

[d] In bielectronic integrals.

[e] This optimization.

[f] Ref. [21].

[g] Ref. [22].

Molecular obitals and orbital energies are obtained by solving ***F***. A monoexcitation-CI process, comprising all virtuals and a sufficient number of non-virtual orbitals to form up to 54 singlets (and 54 triplets, when desired), provides then the spectral quantities.

3. Remarks on Ground State

Although our main interest lies in spectral quantities, some remarks on ground-state results are here in line.

It is well known that HCH-, HCC- and CCC-angles differ somewhat from one alkane to another. Less frequently, however, is it realized that – when re-formulated in terms of hybridization indices (m in sp^m) – this variance is remarkably intensified [23]. Thus, molecular geometries lead to the following C → H hybridizations: methane, 3.00; ethane, 3.28; propane, 3.19 (methyl, 1H), 3.33 (2H) and 3.50 (methylene). Hybridizations in the longer all-*trans* alkanes resemble those in propane, e.g. in anti-butane, 3.22 (1H), 3.33 (2H), and 3.54 (methylene). Conformational effects are illustrated by gauche-butane, 3.38 (methyl, in), 3.44 (out), 3.23, and 3.79 (methylene, in average CCCC-plane), 3.57. Therefore, the assumption that all hybrids are sp^3 and that hybridization is practically conformation-independent, seems unsafe. Indeed, the factor $(1+m)^{-1/2}$, which of necessity occurs in most integrals (frequently in its fourth power), varies in the range 0.24–0.32.

In Table 2, the LCHO orbital energies of methane and ethane are compared with *ab initio* [24–26], as well as with CNDO/2 results (same input geometry, standard parametrization [27]) and with experimental ionization potentials [28]. We consider the comparison relevant because, if an approximate method is designed as a short-cut to certain quantities (spectral here), one would like to know to what extent it simulates *ab initio* [29] and whether it improves on other approximations. The table illustrates that occupied MO's are ordered correctly and that, unlike in CNDO/2, eigenvalues are close to the *ab initio* numbers and obey approximately Koopmans' condition. As for virtual orbitals, reversals sometimes occur; most of the cases encountered concern orbitals that are very close by eigenvalue.

Table 2. Orbital energies in methane and ethane

Symmetry	This work	CNDO/2	*Ab initio*[a]	*Ab initio*	*IP* (PES)[b]
Methane					
t_2	−14.02	−19.81	−13.72	−14.74	13.5–14.5
a_1	−22.65	−34.81	−25.04	−25.36	23
Ethane					
e_g	−12.02	−16.26	−14.01	−13.07	12.0–12.7
a_{1g}	−14.18	−18.56	−14.59	−13.30	13.40
e_u	−15.84	−23.37	−17.07	−16.20	15.0–15.7
a_{2u}	−19.04	−29.39	−23.37	−22.61	20.13
a_{1g}	−24.13	−40.16	−27.32	−27.36	–

Energies in eV.

[a] Methane, Refs. [24, 26], respectively; ethane, Refs. [25, 26], respectively.

[b] Ref. [28].

4. Discussion of Spectra

In the optimization process, two strong absorptions in methane, ethane, and propane, were chosen as target. The data in Tables 3-5 show that this is sufficient to provide a representative outline of the complete spectrum of these molecules, up to 90-100 kK. In addition, such features as the red shift of ethane and propane spectra, with respect to that of methane [31], are reproduced.

Electronic transitions in the three molecules have been discussed extensively [14]. Despite shortcomings inherent in a semiempirical theory, and the exclusion of Rydberg orbitals, our results can contribute to interpretations.

First, departure orbitals and transition symmetries are indicated. For example, the strong absorption - peaking around 75.8 kK - in ethane, has been assigned as E_u, either $e_g \rightarrow a_{2u}$ or $a_{1g} \rightarrow e_u$ [31] or both [14b]. We obtain in this zone two absorptions, one of each type, separated by 2.3 kK. This gap practically coincides with a prediction [14b] based on GTO energy levels [32]. An example of another type is provided by the 88.7 kK peak in propane; between two literature assignments [14c], $a_2 \rightarrow 3p$ and $b_1 \rightarrow 3s$ (B_1), calculations prefer the latter.

Table 3. Electronic transitions (kK) in methane

				Energy	Energy	ϵ (molar)
Sym.	Energy	f	Type[a]	*ab initio*[b]	Exptl.[c]	
A_1	64.9	0				
T_2	78.1[d]	0.07	C	78.50	78.2	5000-6000
T_1	84.4	0				
T_2	85.0[d]	0.24	C	86.33	83.6	5000-6000
E	87.7	0				

[a] See text.
[b] Ref. [30].
[c] Ref. [14].
[d] Used in parameter-optimization.

Table 4. Electronic transitions (kK) in ethane

Sym.	Energy	f	Type[a]	Exptl. and Previous Assignment[b]
A_{2u}	58.2	0.05	C	
E_u	67.2	0.03	D	65[c], 68[d]; $a_{1g} \rightarrow 3s$
E_u ($e_g \rightarrow a_{2u}$)	74.7[e]	0.09	C, D	75.8 ($f \sim 0.3$); either $e_g \rightarrow a_{2u}$
E_u ($a_{1g} \rightarrow e_u$)	77.0	0.12	D	($3p_{\mathrm{sig}}$) and/or $a_{1g} \rightarrow e_u$ ($3p_{\mathrm{pi}}$)
A_{2u}	86.2[e]	0.29	D	87
E_u	88.6	0.11	B	

Only allowed transitions listed.
[a] See text. [b] Ref. [14].
[c] Optical spectrum. [d] Electron scattering.
[e] Used in parameter optimization.

Table 5. Electronic transitions (kK) in propane

Sym.	Energy	f	Type[a]	Exptl. and previous Assignment[b]
A_1	61.4	0.05	C	
B_2 ($b_2 \to a_1$)	62.5	0.03	D, C	64 (weak); $b_2 \to 3s$
B_2	66.2	0.05	C, D	
B_1	67.2	0.03	C	
B_1	70.1	0.03	A	
A_1	73.9[c,d]	0.15	mixed	71.4; $b_2 \to 3p$ and/or $a_1 \to 3s$
A_1	77.7	0.04	D	
B_1 ($a_1 \to b_1$ and $b_1 \to a_1$)	78.2[c]	0.06	D	77.8; $a_1 \to 3p$
B_2	79.0	0.32	B	
B_1	79.4	0.18	A	
B_1 ($b_1 \to a_1$)	88.6	0.05	A	88.7; $a_2 \to 3p$ and/or $b_1 \to 3s$

Weak transitions ($f < 0.02$) not listed.

[a] See text. [b] Ref. [14]. [c] Used in parameter-optimization.

[d] Shifts to 71.4 kK upon extrapolation to full monoexcitation-CI.

Second, a helpful feature of LCHO is that each of the basis orbitals refers to one particular bond, so that MO's are assignable either to skeletal C-C bonding, or to C-H bonds, or as mixed. Correspondingly, one may analyse transitions in terms of four types:

A. CC → CC*

B. CC → CH*

C. CH → CH*

D. CH → CC*

An early theoretical analysis of alkane spectra [33] led to the proposition that, except obviously in methane, the lowest-lying absorptions are localized in the carbon-frame (type *A*), while transitions that involve C-H bonds occur high above the spectral onset. This view has been questioned [31], and our results (Tables 3-5 and below) support the alternative interpretation: in acyclic alkanes, excitation of C-H bonds (types *C* and *D*) comes invariably first. By calculation, the first *A*-type absorption in ethane occurs only above 90 kK. In propane, a CC → CC* transition is computed at around 71 kK, and an extended *A*-region is encountered at 80-90 kK. These features seem to stabilize at the stage of propane. The overall picture is not modified appreciably on chain-lengthening or branching.

4.1. n-Butane

n-Butane is the simplest alkane in which conformational isomerism (apart from methyl rotation) is possible: the energy difference between the gauche-conformer (*g*) and the anti-conformer (*a*) has been estimated as *ca.* 0.7 kcal mol^{-1} [34]. Taking into account the double statistical weight of *g*, this corresponds at room temperature to an *a* : *g* ratio of *ca.* 0.62 : 0.38.

Table 6. Electronic transitions (kK) in butane

Sym.[a]	Energy	*f*	Type[b]	Experimental[c]
A_u	62.6	0.12	*D*, *C*	64 (weak)
A	62.6	0.02	*D*	
B_u	64.3	0.10	*C*	
B	64.5	0.11	*C*	
A	68.8	0.11	*B*, *C*	70 ($\epsilon \sim$ 15 000)
B	70.9	0.04	*A*	
B_u	71.7	0.03	*A*	
A	74.4	0.08	*D*	75 ($\epsilon \sim$ 17 000)
B_u	74.5	0.12	*C*	
B	74.5	0.14	*B*, *C*	
B	76.0	0.08	*C*	
B_u	76.3	0.02	*C*	
B	77.1	0.11	*C*	
A_u	77.2	0.03	*B*	
A	77.9	0.07	*B*	
B_u	78.1	0.17	*A*	
B	78.1	0.06	*A*	
A_u	78.4	0.03	*D*	
B	78.6	0.06	mixed	
B	78.8	0.10	*D*	
A	79.6	0.03	mixed	80–86
B_u	82.1	0.12	*A*	(ϵ 20 000 $\sim$ 25 000)
B_u	83.0	0.25	*A*, *B*	
A_u	83.6	0.11	*B*	
A	84.9	0.04	mixed	
A_u	85.6	0.10	*D*	
B	87.3	0.07	mixed	
B_u	87.5	0.18	*A*	

Weak transitions ($f < 0.02$) not listed.

[a] Transitions A_u and B_u are of anti-conformer; transitions A and B - of gauche-conformer.

[b] See text.

[c] Ref. [31]. Extinctions estimated from curve.

The spectrum of butane has been recorded [31], but its interpretation not carried far, presumably because of the conformational variety. We started by calculating both conformers (Table 6). The general pattern is conserved, subject to conformation-dependent modifications. In the conformer of high symmetry (*a*), the 75 kK band is composed mainly of transitions with "pure" regional character, that is, CH → CH* (*C*) and CC → CC* (*A*); as for the 85 kK band, most contributors to it originate at the carbon-frame, and are either "pure" (CC → CC*, *A*) or of the "transfer" type (CC → CH*, *B*). In the conformer of low symmetry (*g*), the regional character is practically lost. Also, and in distinction with the anti-form, the 75 band is computed as more intense than the 85 kK band.

In order to check the computed numbers against the experimental absorption curve, we first weighted by population the oscillator strength of the 39 allowed transitions (14 of *a*, 25 of *g*, not all listed in Table 6) computed in the range 62-88 kK. We then grouped them in four bands and, following Jørgensen [35], examined the five-parameter function

$$S(\nu) = k \sum_i \sum_j \frac{f_{ij}}{d_i} 2^{-[(\nu-\nu_{ij})/d_i]^2}$$

Here, i varies over the (four) bands, j varies over all transitions in band i; f_{ij} and ν_{ij} are, respectively, the oscillator strength and frequency of the computed transition j in i, and the scale factor k represents conversion from f to ϵ [theoretical value $(4.32 \times 10^{-6})^{-1} = 2.31 \times 10^5$]. Band half-widths d_i were taken to depend only on the spectral range (evidently, more versatility could be obtained by letting them depend on conformation as well). By minimizing $\Sigma(\nu)[\epsilon(\nu) - S(\nu)]^2$, the following were obtained: $d_1 = 17.54$ kK (range 62-65 kK), $d_2 = 1.82$ (68-72), $d_3 = 7.14$ (74-80), $d_4 = 5.88$ (80-88 kK). In bands 2-4, d-values are of the expected order of magnitude [35]; band 1, however, is computed too wide.

In Fig. 1, $S(\nu)$ is plotted (with $k = 1.8 \times 10^5$) against the experimental spectrum. It is interesting to note that two peaks (64 and 75 kK), although located correctly in the calculation, "disappear" in the plot. Obviously, shortcomings in the evaluation of oscillator strengths (Sect. 1) account for this, as well as the conformation-independent construction of d-values.

4.2. Isobutane

As a prototype of branched chains, we computed isobutane (Table 7). Here also, calculation rationalizes experimental findings, e.g., the hyperchromic shift, with respect to the spectrum of normal butane [36], is reproduced. It also confirms [14] that branching should not affect much the location of spectral bands. A noticeable difference with unbranched alkanes is that, up to 90 kK, the contribution of B-type excitations is estimated as relatively small.

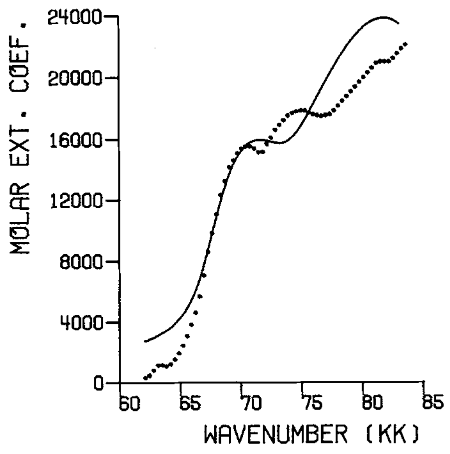

Fig. 1. Theoretical (———) and measured (· · ·) [31] spectrum of normal butane

Table 7. Electronic transitions (kK) in isobutane

Sym.	Energy	*f*	Type[a]	Experimental[b]
A_1	62.7	0.05	*C*	60-65
E	65.8	0.01	*D*	
A_1	71.8	0.14	*A*	70
E	72.5	0.02	*A*	
E	73.8	0.02	*B*	
E	76.7	0.01	*C*	
E	77.3	0.24	*C*	75
E	78.7	0.04	*C*	
A_1	78.8	0.07	*C*	
E	79.1	0.02	*C*	
A_1	79.7	0.08	*D*	
E	81.0	0.02	*B*	
E	87.3	0.13	*A*	86.5

Weak transitions ($f < 0.01$) not listed.
[a] See text.
[b] Ref. [33].

5. Conclusion

We have described a semiempirical SCF-CI MO technique to calculate spectral quantities in compounds of carbon and hydrogen. Results for five molecules have been discussed.

We consider of particular interest the analysis of butanes (Tables 6, 7, and Fig. 1), which is indicative of what one could do in investigating higher alkanes. Unlike others [14d], we do not think that the situation here is "hopelessly complicated". There are non-costly theoretical procedures, molecular-mechanical [15] and quantum-mechanical [37], of identifying minimum-energy conformers of a molecule and estimating their relative energies. A method, even of the type discussed here, could then be used to compute spectral transitions in each, and - by appropriate weighting - resolve the experimental spectrum.

Actually, the situation could turn out much simpler than it seems. First, we have checked that hybridization indices practically stabilize at the stage of butane. Geometrical detail, for the higher alkanes, is therefore estimable from data on anti- and gauche-butane, isobutane, and neopentane [$m(C \rightarrow H) = 3.30$]. Second, the conformations of higher alkanes can be built up, and their energies obtained to a good approximation, by a sum-rule [38]. Third, the derivation of molecular orbitals can be simplified: as expected [6], $\boldsymbol{P}$-elements are practically transferable from one molecule to another, e.g., $P(C–C) \sim 0.98$, $P(C–H) \sim 0.98$, $P(H \ldots H, \text{geminal}) \sim 0.11$, and so on. Matrix $\boldsymbol{G}$ can therefore be written down by inspection, and the iterative SCF process replaced by a single diagonalization of $\boldsymbol{F}$.

On the other hand, further elaboration of the scheme is envisageable: Rydberg orbitals could be inserted, the formulation refined, etc. Semiempirical methods have been found useful in correlating the spectra of unsaturated structures. It is our belief that the extension of such approaches to molecules in general would prove worthwhile.

Appendix: Parameters

Following Freed's analysis [39], we concentrate upon the effective core Hamiltonian $\boldsymbol{H}$. In standard notation, $\boldsymbol{F} = \boldsymbol{C}\boldsymbol{\epsilon}\boldsymbol{C}^{\dagger} = \boldsymbol{H} + \boldsymbol{G}$, so that

$$\boldsymbol{H} = \boldsymbol{C}\boldsymbol{\epsilon}\boldsymbol{C}^{\dagger} - \boldsymbol{G} \tag{1}$$

and, as long as CI is disregarded,

$$\Delta E(k \to l) = \epsilon_l - \epsilon_k + K_{kl} - 2J_{kl} \tag{2}$$

We start with a hydrogen-1s exponent of 1 (for the evaluation of bielectronic integrals), and other parameters = 0. In methane, only two different numbers, H_{ii} (hydrogens, 1s) and H_{ii} (carbon, sp^3), occur on the diagonal of $\boldsymbol{H}$. Pairs of these numbers were scanned until a ground-state calculation produced "reasonable" overlap and atomic orbital populations. The initial $\boldsymbol{C}$, and therefore $\boldsymbol{G}$, are thus established. Identifying $\Delta E(k \to l)$ with the *ab initio* transition energies [30] and the two ϵ_k with the experimental ionization potentials [28], values for the two ϵ_l (Eq. (2)) and for $\boldsymbol{H}$ elements can be written down.

In principle, if the functional interdependence of $\boldsymbol{H}$ elements and the parameters has been decided upon, starting parameter-values are available at this stage. In practice, we tried a number of possible formulations. Among those examined, the formulation of Sect. 2 performed best.

Final parameter values, under the chosen formulation, were arrived at by a pattern-search optimization [40] of SCF-CI transition energies. As target we took six electronic transitions (methane, 78.2 and 83.6; ethane, 75.8 and 87; propane, 71.4 and 77.8 kK). No restrictions were imposed at this stage on any other quantity.

The pattern-search technique has also been used to derive optimal d-values (Sect. 4).

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