Theoret. Chim. Acta (Berl.) 50, 313–316 (1979)

THEORETICA CHIMICA ACTA

HAM/3: An Algorithm or a Theory?

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The theoretical basis of the semiempirical HAM/3 MO method, recently introduced by Åsbrink *et al.*, has been the subject of some discussion. We propose to regard the method's energy expression as a hypothesis, and mention a few implications of this proposal.

Key words: HAM/3 method

1. Documents in the Case

1) Åsbrink, Fridh and Lindholm [1] introduce a new semiempirical MO-method, HAM/3. Their results are in good agreement with experimental data, and the expense in terms of computer time is small. They claim that the method is based on a correct treatment of the correlation and the self-repulsion.
2) De Bruijn [2] examines the theoretical part of [1] and denies that it is even approximately correct.
3) Chong [3] confirms the two computational advantages reported by Åsbrink, finds my comments [2] partly valid but overcritical, and is dissatisfied with the large numbers of parameters used in HAM/3.

2. HAM/3: the Theory

There are several topics of discussion; for convenience we follow the numbering given in section 3 of [3].

1. There is no disagreement between Chong and me concerning the HAM/3 treatment of the atomic correlation energy: it is not formally correct, but the proposed formula gives a uniformly excellent fit with the experimental results.

0040-5744/79/0050/0313/$01.00

2. Chong's second statement under this heading is correct: contrary to my interpretation in [2] Åsbrink does not use ground state ζ's throughout his calculation.

(4) and the rest of (2) concern a screening problem and molecular correlation, respectively. Because HAM/3 attempts to incorporate the correlation in terms of screening the two subjects can be combined.

Chong accepts my statement that the occurrence of $(P_{\mu\mu}-1)$ in the expression for the screening of an electron in orbital μ leads to unphysical consequences; he states that instead of $P_{\mu\mu}-1$, $P^{\beta}_{\mu\mu}$ should be used for the calculation of the screening of an α-electron in μ. I do not accept this formula either, nor, in fact, any other expression involving only one-particle densities.

Whenever there is an electron in spinorbital $\mu^{\alpha}_{\mathrm{A}}$ (probability: $P^{\alpha}_{\mu\mu}$) it is screened from nucleus A by the *instantaneous* charge on A, minus itself, and not by a *constant* charge, as in the atomic case. When there is no electron in μ^{α} there is nothing to screen. So the average correction for all *relevant* configurations is -1; unfortunately we do not know the expression to which the correction should be applied. The word "instantaneous" implies that the problem must be formulated in terms of many-particle density matrix elements, and I do not see that it can be reduced to an *a priori* correct formula in terms of one-electron densities. How about an *a posteriori* correct formula, i.e. an expression which is justified by its reproduction of all relevant results? This has not been performed or attempted, and my example [2], comparing two states of H_2, makes me doubt whether it is at all possible.

Anyway, Åsbrink c.s. regard their expression for F_{pq}, which is supposed to account for the molecular correlation energy, as an assumption, and we can do the same, though without sharing their confidence in its correctness, because of the serious incompleteness of the analogy with the atomic correlation problem.

3. My doubts concerning the correct number of two-electron interactions have their origin in the term $\sum_{\mathrm{A}<\mathrm{B}} Q_{\mathrm{A}} Q_{\mathrm{B}} \gamma_{\mathrm{AB}}$, which accounts for the electrostatic interaction between net charges on the atoms. Actually this term gives rise to three problems: the consistency of the HAM/3-theory is imperilled by its presence, its form and its evaluation.

a) We agree with Chong's opinion that one is led to regard the HAM/3 energy as the negative of the kinetic energy. However, why does one potential energy term survive the operation of the virial theorem, and why should it be this particular term? Can the virial theorem be applied to a part of the molecular energy?

b) In so far as the electrostatic interactions in ε_i [2] can be made explicit – and I need nothing but the HAM/3 expressions for the matrix elements and a generally valid formula for eigenvalues – they appear to account for the repulsion of an electron by $2n$ electrons; this must happen, because $P_{\mu\mu}$ is the one-particle density term for an ensemble of $2n$ electrons. I do not think that this elementary analysis transcends the boundaries within which the HAM/3 language can be used.

Whatever is implicit in the γ's, the appearance of $2n$ repulsions in a theory which claims explicitly to have eliminated the fictitious interactions is surprising.

c) The AO basis used in HAM/3 obviously consists of non-orthogonalized orbitals, and in most stages of the analysis the overlap integrals are explicitly considered. In the evaluation of $\sum Q_A Q_B \gamma_{AB}$, however, parametrization methods and numbers are borrowed from NDO-methods, for which orthogonalized orbitals form the appropriate basis. Also, in a non-othogonal basis there are non-zero charges in the bonds. It is not clear why their electrostatic interactions with each other and with the atomic charges are ignored, contrary to the atom–atom repulsions.

3. HAM/3: the Algorithm

Hitherto the applications of the HAM/3 computational method resulted in a considerable number of consistently good results, which must not be disregarded. On the other hand the many discontinuities and uncertainties in the derivation of the final formulas do not enable us to regard them as correct. Therefore we suggest that the HAM/3 algorithm – i.e. the formulas for the elements of $\boldsymbol{F}$, the parameter values, and the identification of experimental energy differences with $\Delta\varepsilon$'s – should be regarded as a hypothesis. The implications are:

a) Like any other hypothesis HAM/3 should be subjected to as many tests as possible. Each success contributes to our confidence in its correctness, though one failure is enough to cause serious doubt.

b) If an abundancy of good results leads us to accept that the HAM/3 algorithm is substantially correct, then we may conclude that all relevant energy terms are represented, explicitly or implicitly, by the formulas and the parameters. However, even then it does not follow that correlation and electron–electron interaction are correctly accounted for by the terms specified in Åsbrink's paper. This is just a matter of logic: the correctness of a conclusion can not be invoked to justify any individual step in an argument from which the conclusion is derived.

c) In tests and applications of the algorithm we should be aware of a peculiar difficulty, due to the introduction of the virial theorem at an early stage of the derivation. Elaborating one of Chong's remarks, we note that the virial theorem in the simple version $\langle H\rangle \equiv \langle T\rangle + \langle V\rangle = -\langle T\rangle$ can be used only in the molecule's equilibrium configuration. The configuration referred to can be no other than the one predicted by the approximate or correct energy expression actually used, and by the condition that for each coordinate R_i $\delta\langle H\rangle/\delta R_i = 0$, or $\delta\langle T\rangle/\delta R_i = -\delta\langle V\rangle/\delta R_i$. In HAM/3, however, we have expressed the energy all the time as $-\langle T\rangle$, and we know nothing about $\langle V\rangle(R_i)$. Consequently, the configuration to which HAM/3 may be applied can not be defined within the terminology of the method. We have to assume either that we make no additional approximation by using HAM/3 for molecules in their *experimental* equilibrium configuration, or that any approximation inherent to our choice of this configuration is accounted for by the parameters. It seems to be impossible to decide in favour of either assumption.

4. Formalism, Parameters, and the Reasons for Criticism

Though Chong defends HAM/3 for the sake of its computational performance, he accepts my refutation of one alleged correct step in the derivation, and his acceptation of the working formulas of the method does not imply that he regards the corrections of other steps in the derivation as proved; the emphasis in his discussion is on the possibilities for fitting the chosen expression so as to reproduce experimental data. In my opinion this is an acceptable description of the status of HAM/3, but it implies two good reasons for my earlier comments [2]:

1. Åsbrink c.s. offer a simple general treatment of some difficult problems, which is apparently supported by their numerical results. At the very least it is not proved that the proposed formulas are sufficient for a correct treatment of the correlation and the two-electron terms separately. Uncritical further applications of their ideas should be prevented.
2. The published intuitive derivation of the HAM/3 procedure should be replaced by one that is as rigorous as possible, i.e. a derivation in which all approximations and simplifications are well defined. Then we could decide whether the HAM/3 algorithm is universally correct, or whether there are inherent weaknesses which lead to unreliable results under specified conditions. The knowledge of such restrictions is a matter of considerable importance in connection with a method which can be applied to large molecules, where a check by means of better defined theoretical methods is impossible.

Such a consistent derivation may incorporate an argument that meets some of Chong's objections against the liberal use of parameters. One unusual feature of HAM/3 is its use of different ζ's for intra-atomic and interatomic interactions. According to an analysis by Cusachs and Corrington [4] it is possible and advisable to compensate for the deficiencies of a single ζ Slater AO by using different AO's, chosen by means of a well-defined method, in the calculation of expectation values which depend mainly on the behaviour of the wavefunction in the neighbourhood of the nucleus, in the outlying regions of the atom, or in the whole atomic region.

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Received September 11, 1978