CASE STUDIES OF SOME ATOMS-IN-MOLECULES FORMULATIONS

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Dedicated to Academician O. Wichterle on the occasion of his 70th birthday.

Four versions (Hermitian, non-Hermitian, Schmidt- and symmetrically orthogonalized) of the atoms-in-molecules method are applied to calculate potential energy curves of the H_2, HeH and HF species. By comparing the results of various approaches among themselves and to external accurate data, conclusions are drawn concerning the reliability of the individual solutions.

Among methods which seem to be particularly suited to calculation of potential energy surfaces (PES's) for chemical dynamics studies, two approaches play an important role: the methods of "diatomics-in-molecules" (DIM)[1-3] and "atoms-in- molecules" (AIM)[4,5]. The main reason for this is that both methods display correct behaviour upon separation of the system into atomic fragments at relatively low computer-time consumption. The DIM method, in addition, ensures correct dissociation limits for any combination of diatomic fragments. These properties of both methods follow from exploitation of proper external data concerning atomic and, in the DIM case, diatomic energy levels. From both methods the AIM one is less semiempirical in that it introduces only atomic corrections, preserving its "absolute" character by calculating molecular integrals similarly as in any other *ab initio* treatment. Thus, the AIM method requires considerably more computational effort to apply than the DIM method, making calculation of PES's for larger systems very difficult. Because in both methods polyatomic basis functions are generated by coupling together proper eigenfunctions for various states of constituent atoms and because of common atomic dissociation limits, it seemed to be natural to join advantages of the AIM and DIM methods to obtain a reliable and predictive means for calculating PES's. The relationship between these methods can be logically established by using the AIM method as a source for diatomic information needed as input for DIM calculations. This motivation lay in foreground when starting a project on to find out how well the AIM method[6-10] is able to yield excited state properties (of diatomic species). However, the impact of the answer reached beyond that goal, since many processes do need for their microscopic interpretation knowledge of elec-

tronically excited molecular levels (Penning and associative ionization, atom–atom collision processes etc.).

In the course of understanding the AIM method various views on this method appeared. Naturally enough, there have also been disappointments which have been connected with the failures of the method. New hopes arose when − in comparison with the original suggestions of Moffitt[4] − new ways of introducing atomic corrections[5] and the deteriorating effect of the hermitization step[11,8] within the standard AIM procedure were observed. Because some previous conclusions, concerning relationships between various AIM formulations, were drawn on the basis of simple model systems, we promised[8] to bring evidence on the reliability of the improved AIM versions by application to more complex systems. Therefore, we examine in the present paper the use of the symmetrically orthogonalized[8] and non-Hermitian AIM approaches[11] applied to H_2, HeH a HF atomic species. Particularly, we compare the results with those previously obtained by other methods, attempting to understand and rationalize the effects related to various AIM formulations.

THEORETICAL

Moffitt's AIM method[4,5] is based on the assumption that the wave function of a molecule can be constructed from the eigenfunctions $\psi_{\alpha i}^A$, $\psi_{\beta i}^B$, ... associated with the states α_i, β_i, ... of separate atoms A, B, ..., satisfying

$$\mathbf{H}^A \psi_{\alpha i}^A = E_{\alpha i}^A \psi_{\alpha i}^A , \qquad (1)$$

where $\mathbf{H}^A$ is the atomic Hamiltonian and $E_{\alpha i}^A$ the exact (e.g. experimental) energy of the given state. The functions $\psi_{\alpha i}^A$ provide a polyatomic basis set of composite functions (CF's) defined in terms of an antisymmetrized direct product

$$\psi_i = \mathbf{A}\psi_{\alpha i}^A \psi_{\beta i}^B ... , \qquad (2)$$

where the antisymmetrizer $\mathbf{A}$ allows for the interchange of the various electrons originally assigned to the separate atoms. This type of basis set is common to both AIM and DIM methods.

The total molecular wavefunction can then be expressed as

$$\psi = \sum_i C_i \psi_i \qquad (3)$$

with the coefficients C_i serving as variational parameters. The functions ψ_i are nonorthogonal, leading to the so-called nonorthogonality problem of the valence bond theory.

With regard to the form of the wave function [cf. Eqs (2) and (3)] it is convenient to define a decomposition of the electronic Hamiltonian for the total molecule:

$$\mathbf{H} = \mathbf{H}^A + \mathbf{H}^B + ... \mathbf{V}^{AB} ... , \qquad (4)$$

where the operator $\mathbf{V}^{BA}$ represents interatomic electron-electron and electron-nucleus interaction terms. This decomposition can be accomplished because specific electrons are initially attributed to atoms A, B .....

The action of Hamiltonian (4) on basis functions (2) can be exemplified by giving Hamiltonian matrix elements[4,5] for the case of a diatomic molecule:

$$H_{ij} = \left(E_{\alpha j}^A + E_{\beta j}^B\right)\langle\psi_i\,|\,\psi_j\rangle + \langle\psi_i\,|\,\mathbf{V}^{AB}\,|\,\psi_j\rangle\,, \tag{5a}$$

$$H_{ji} = \left(E_{\alpha i}^A + E_{\beta i}^B\right)\langle\psi_j\,|\,\psi_i\rangle + \langle\psi_j\,|\,\mathbf{V}^{AB}\,|\,\psi_i\rangle\,, \tag{5b}$$

where use is made of Eq. (1). Since the evaluation of the term $\langle\psi_i\,|\,\mathbf{V}^{AB}\,|\,\psi_j\rangle$ is rather complicated, Moffitt[4] suggested an indirect way of calculating this quantity by means of the relation

$$\langle\psi_i\,|\,\mathbf{V}^{AB}\,|\,\psi_j\rangle = \langle\psi_i\,|\,\mathbf{H}\,|\,\psi_j\rangle - \left(\tilde{E}_{\alpha j}^A + \tilde{E}_{\beta j}^B\right)\langle\psi_i\,|\,\psi_j\rangle =$$
$$= \tilde{H}_{ij} - \left(\tilde{E}_{\alpha j}^A + \tilde{E}_{\beta j}^B\right)\tilde{S}_{ij}\,, \tag{6}$$

where

$$\tilde{E}_{\alpha j}^A = \langle\psi_{\alpha j}^A\,|\,\mathbf{H}^A\,|\,\psi_{\alpha j}^A\rangle \tag{7}$$

is the theoretical energy value corresponding to the state α_j of atom A, calculated with the approximate atomic wave function $\psi_{\alpha j}^A$. The advantage of using Eq. (6) lies in the fact that the expressions appearing in the rhs. of Eq. (7) are easier to calculate than the term $\langle\psi_i\,|\,\mathbf{V}^{AB}\,|\,\psi_j\rangle$. Further, in Eq. (7) we introduce a convention that all quantities calculated using orbital-type wave functions are denoted by a tilde. On inserting (6) in Eq. (5), we obtain

$$H_{ij} = \left(\Delta E_{\alpha j}^A + \Delta E_{\beta j}^B\right)\tilde{S}_{ij} + \tilde{H}_{ij}\,, \tag{8a}$$

$$H_{ji} = \left(\Delta E_{\alpha i}^A + \Delta E_{\beta i}^B\right)\tilde{S}_{ij} + \tilde{H}_{ij}\,, \tag{8b}$$

where the symbol $\Delta E_{\alpha i}^A$ denotes the difference between the experimental and computed energy values for atomic state α_i and the hermiticity of the matrix $\mathbf{H}$ is employed. We note that $\mathbf{H}$ is generally a non-Hermitian matrix. From Eq. (8) we descend now to four modifications of the AIM method which are applied in the next section to particular systems:

1) *Hermitian formulation* (denoted by H). The conventional solution corresponding to Eq. (8), originally suggested by Moffitt[4], consists in its hermitization via

$$H_{ij}^H = \tfrac{1}{2}\left(H_{ij} + H_{ji}^*\right)\,, \tag{9}$$

where an asterisk denotes a complex conjugate quantity.

2) *Non-Hermitian formulation* (NH). The direct solution of a non-Hermitian secular equation of type (8) has been used in a number of problems[12,13] and recently applied to AIM equations[11,8].

3) (*Schmidt-*) *orthogonalized formulation* (OM). The atomic corrections are applied to Hamiltonian matrix elements

$$H_{ij}^0 = \tilde{H}_{ij}^0 + \left(\Delta E_{\alpha i}^A + \Delta E_{\beta i}^B\right)\delta_{ij} \tag{10}$$

expressed in terms of an orthonormalized basis ψ^0 associated with the original basis via transformation,

$$\psi^0 = \psi\mathbf{T}^0\,, \tag{11}$$

where δ_{ij} is the Kronecker symbol, index 0 denotes connection with orthogonalized functions and use is made of the notation of Montet, Keller and Mayer[14]. The arbitrariness in choosing the type of orthogonalization was removed by Balint–Kurti and Karplus[15] who suggested to apply the Schmidt procedure to the functions ψ_i ordered in accordance with increasing absolute values of the correction $(\Delta E_{ai}^A + \Delta E_{\beta i}^B)$. This type of approach is called the orthogonalized Moffitt (OM) method.

4) *Symmetrically orthogonalized formulation (SOM)*. Because the symmetric (Löwdin) orthogonalization[16] preserves the maximum similarity to the original basis set, the SOM version of the AIM method was proposed[8] as an alternative to the OM method.

For comparison, results of those calculations are also presented which are based on the same set of functions ψ_i, however with zero atomic corrections. Such calculations are referred to as VB calculations.

All four versions of the AIM method mentioned above are simple enough to be applicable to larger systems without computational difficulties. This is the main reason why we leave here out of consideration those modifications of the AIM method which have to undergo a more elaborate solution (for details, *cf.* ref.[8]).

RESULTS AND DISCUSSION

Since general aspects are most transparent in simple cases, we examined in our former paper[8] the above mentioned AIM approaches by their application to a two-dimensional model system, consisting of covalent and ionic structures of the ground state of the H_2 molecule. The restricted form of the approximate wave function gave us an opportunity to express the energy partitioned with regard to the individual AIM approaches and enabled us to make a number of useful conclusions concerning the behaviour and interrelation of various AIM formulations. For more complex systems no direct way of providing this information exists and it is the purpose of this and an other previously submitted paper[10] to bring a portion of insight into understanding of the methods when applied to general cases.

Our further attention will be devoted to that AIM results on potential energy curves (PEC's) concerning three diatomic species: H_2, HeH and HF. As atomic orbitals (AO's), used for the construction of approximate atomic eigenfunctions, the $1s$, $2s$ and $2p$ orbitals optimized for the ground state of the neutral atoms are used. The electronic states of ionic species are built up from the same AO's. Each AO is expressed in the form of a contracted gaussian function; details on the corresponding exponents and contraction coefficients for the AO's of the He, F a H atoms, and the specification of the approximate atomic eigenfunctions together with the atomic correction terms can be found in previous publications[6–8].

H_2 *molecule*. Because the four lowest electronic states of H_2 belong to Σ symmetry[17], we restricted our considerations to this symmetry species. Proper combinations of hydrogen atomic states corresponding to occupancy of the $1s$, $2s$, and $2p$ AO's, and of ionic states H^+ and H^- (^1S_g, ground state), yield a 24 CF basis set

spanning diatomic states of this symmetry

$$\left[8\,^1\Sigma_g^+\,, \quad 7\,^3\Sigma_u^+\,, \quad 3\,^3\Sigma_g^+\,, \quad 4\,^1\Sigma_u^+\,, \quad ^3\Sigma_g^-\,, \quad ^1\Sigma_u^- \right].$$

For the $1s$, $2s$, $2p$ (H) and H$^-$ states the energy correction terms $\left(-\Delta E_i^{\mathrm{H}}\right)$ amount to 0·0027, 0·0052, 0·0118 and 0·1519 a.u.[5,6,8], respectively, provided the electronic state of H$^-$ is described by a single determinant function — this correction scheme will be referred to as case 1. We notice that the correction for H$^-$ differs by more than one order of magnitude from the other correction terms. Since it was shown[8] that the effective correction terms appurtenant to various AIM formulations depend strongly on the difference between atomic corrections, it seemed both interesting and useful to provide a means for varying the amount of discrepancy between the atomic correction terms. This can be simply achieved by introducing a "better" function for approximating the H$^-$ state: a four-fold configuration interaction wave function, consisting of (one-centre) structures $(1s)^2$, $(2s)^2$, $(1s\,2s)$ and $(2p)^2$, becomes with the correction term $\left(-\Delta E^{\mathrm{H}^-}\right) = 0\cdot0197$ a.u. rather close to the values of neutral hydrogen atomic corrections. The use of the improved description of the H$^-$(^1S_g) state characterizes the correction scheme 2 in calculating AIM PEC's. Because the H$^-$(^1S_g) atomic state occurs in a single VB structure, the change in the correction scheme affects just those states including the H$^+$H$^-$ structure with a significant weight. Also, in these cases, substantial differences between the results of various versions of AIM calculations performed within the correction scheme 1 can be expected.

Figs 1a and 1b give results for the H$_2$ $^1\Sigma_g^+$ ground state, as obtained by various AIM formulation in using both descriptions of the H$^-$ state, and by an accurate calculation of Kołos and Wolniewicz[18]. The VB curves are drawn to dissociate to experimental atomic energies. By comparing the AIM PEC's with those previously obtained[8] for the approximate wave function of Weinbaum type[19], we can conclude that the distinct behaviour of the individual AIM solutions remains the same as deduced from the analysis of the two-dimensional model. Practically it holds that the OM and H AIM versions represent, with a portion of reservation[8,10], the higher and lower limits, respectively. The NH and SOM PEC's are, roughly speaking, embedded within these limits. In other words, if the OM and H energy values come close together, the remaining formulations (SOM and NH) only corroborate the results. Further, within the two-dimensional model it was shown[8] for the ground state PEC that the hermitization process, involved in the H formulation, brings about a lowering of energy with respect to the non-Hermitian one. Under certain conditions, this factor can lead to a total breakdown of the H formulation, as it is documented in Fig. 1a. This failure of the H formulation is connected with the fact that at short internuclear distances the H$^-$H$^+$ structure becomes a significant contribution to the ground state wave function. If approximately equal corrections apply to different
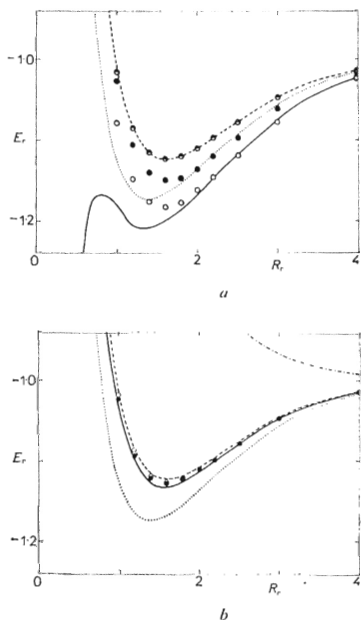
a

b

Fig. 1

Comparison of PEC's for the ground state of H_2 as obtained by various AIM formulations (H, solid curve; OM, broken curve; NH, ●; SOM, ○; VB, ◒; the same notation is preserved throughout the paper) and *ab initio*[18] calculation (dotted curve). *a*) AIM calculations using correction scheme 1. *b*) AIM calculations using correction scheme 2. The dashed-dotted curve is used for the $^3\Sigma_u^+$ state; all versions yield almost identical results. Distances and energies are expressed as relative quantities $R_r = R/R_0$ and $E_r = E/E_0$, respectively, with $R_0 = 0.052917$ nm and $E_0 = 4.35942 . 10^{-18}$ J, throughout the paper. In the text these quantities will be referred to as atomic units (a.u.)
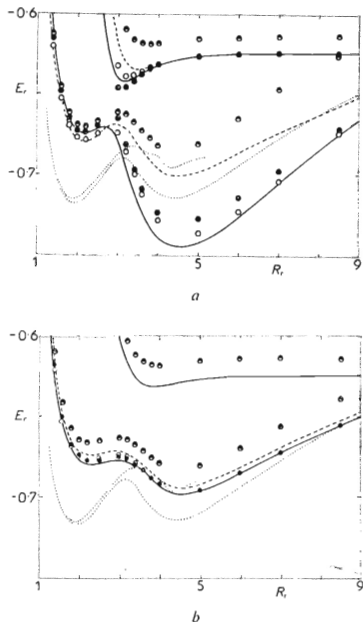
Fig. 2

Comparison of PEC's for the first and second H_2 excited states of $^1\Sigma_g^+$ symmetry as obtained by various AIM formulations, *ab initio* calculations (dotted) of Gerhauser and Taylor[20] (higher curve), and Kolos and Wolniewicz[21] (lower curve). *a*) AIM calculations using correction scheme 1. *b*) AIM calculations using correction scheme 2; for the higher state all versions yield almost identical results

states, then various AIM versions yield results without significant differences in the PEC's($cf.$ Fig. 1b), and shrink together for completely equal correction terms for all interacting states.

Because the $H^-(^1S_g)\,H^+$ CF contributes only to molecular wave functions of $^1\Sigma_g^+$ and $^1\Sigma_u^+$ symmetries, the $^3\Sigma_u^+$ state, shown in Fig. 1b, is, from the viewpoint of changing the H^- state description, of no interest. However, it brings further evidence that various AIM modifications lead to almost identical results, if the application concerns unbound states ($cf.$ also ref.[6,7]).

In the AIM ground state wave function, the single (two-centre) $1s1s$ configuration plays a dominant role within a wide interval of interatomic separations (for all AIM versions and both correction schemes above about 1.7 a.u.). This simple situation is dramatically changed in the two lowest excited states of $^1\Sigma_g^+$ symmetry, as it is implied by the complex shape of the PEC's shown in Fig. 2.

The double-minimum character of the first excited $^1\Sigma_g^+$ state has already been recognized in the early sixties both theoretically[22] and experimentally[23]. According to our AIM results, both lowest excited $^1\Sigma_g^+$ states can be interpreted in term of four significantly different ranges of internuclear distances. Concerning the first excited PEC, the inner minimum (first) and asymptotic (fourth, above 16 a.u.) regions are dominated by the (two-centre) $1s2s$ configuration, the outer minimum (second; up to about 8·5 a.u.) and third (surrounded by the second and fourth) regions are characterized by the ionic H^+H^- configuration and by the mixture of $1s2s$ and $1s2p$ structures, respectively. Consistently, the second excited state is predominantly a mixture of $1s2p$ and H^+H^- structures in the first region, switching to a mixture of $1s2s$ and $1s2p$ configurations in the medium range and turning to a pure $1s2p$ state at approaching the asymptotic region of separated atoms. The interchange of the dominant structures, describing the first excited state, indicates the existence of two avoided crossings occurring approximately at internuclear separations 4 and 8·5 a.u. The general features of these states are also reproduced by the VB calculations which — in contrast to Fig. 1 — are in Fig. 2 and further figures (with the exception of Fig. 6b) not corrected with regard to experimental dissociation limits. Also, the regions of avoided crossing correspond to those which were obtained by accurate ab $initio$ calculations[20,21]. However, the quantitative agreement between the AIM and ab $initio$ results is unsatisfactory; curiously enough, the depths of the inner and outer minima come out in the reverse order. In accordance with our previous observations and conclusions we notice that the amount of the ionic structure in the wave function determines the degree of the energy variation due to the change both in the correction scheme (altering the H^- description) and kind of AIM formulation. Particularly, the most pronounced discrepancy among various AIM versions occurs with the second excited state in the first region, and with the first excited state in the second region of internuclear distances ($cf.$ Fig. 2a). It is also noteworthy that in such cases PEC's produced by various formulations for the same state can inter-

sect. Further, for the excited states (in contrast to the ground state) no restriction concerning the order of the H and NH energy values holds; notice, *e.g.*, that at the minimum of the second excited state the NH version yields lower energy values than the H version.

In Fig. 3 we present AIM PEC's for the lowest $^1\Sigma_u^+$ state. Because of the large contribution of the ionic configuration H^+H^- to the wave function within a broad interval of internuclear separations, in using correction scheme 1 a discrepant pattern of curves is obtained. We note that the comparative PEC of Kołos and Wolniewicz[24] lies in between. At short distances, however, the AIM PEC's are too steep, indicating that an insufficient number of configurations is taken into account. This is, of course, a common shortcoming to all our AIM calculations using a restricted basis set. At increasing internuclear separation the wave function converges to the $1s2p$ configuration. Since the state under consideration is the lowest one of given symmetry, all conclusions concerning the relationships between various AIM versions, reached on the basis of studying the ground state of H_2, hold for this case too.

The final example on electronic states of H_2 in our series of calculations concerns the lowest $^3\Sigma_g^+$ state. From the AIM calculations it comes out that the $1s2s$ configuration is the major one at shorter internuclear separations, while the $1s2p$ configuration becomes dominant at about 8·5 a.u. and represents the dissociation limit. Fig. 4 shows the calculated PEC's compared with accurate *ab initio* calculations[20,24].

The same purpose serve also complementary calculations on some of the states of the species HeH and HF. Earlier, we have performed H and OM calculations on HeH[6] and HF[7] systems in order to obtain input information for a subsequent DIM calculation on triatomic systems. In this paper we complement the existing AIM results by NH and SOM data which are intended to corroborate our understanding of the relationships betwen the individual AIM versions. The remaining figures yield further evidence that interpretation similar to that met in previous AIM treatments can be applied even in cases of HeH and HF.

HeH molecule. The calculated PEC's for the $^2\Sigma^+$ ground and first excited stated of HeH are shown in Fig. 5. The H and SOM ground state curves are found to possess a spurious minimum between 3 and 4 a.u. (*cf.* ref.[6]) and, in exaggerating the lowering of the calculated molecular energy, this pattern resembles the case with H_2 in Fig. 1*a*. However, the NH and OM PEC's behave reasonably in a wide range of internuclear separations, including the prediction of the existence of a van der Waals minimum at R_r of about 8·5 a.u. with the size of 2·2 . 10^{-6}, 2·6 . 10^{-6} and 2·2 . 10^{-6} a.u. for VB, OM and NH versions, respectively. Because the $^2\Sigma^+$ higher excited states are implicated in many avoided crossings, the pattern of the PEC's obtained with different AIM formulations becomes rather intricate and is, therefore, omitted.

HF *molecule.* Since among the variety of Σ and Π states studied previously[7] only the two lowest $^1\Sigma^+$ states exhibit marked differences in the H ond OM results, the

ground and $^1\Sigma^+$ first excited states have become a subject of our renewed interest with regard to testing the extended collection of AIM formulations. In Fig. 6 the AIM results are plotted along with the RKR potential curves of di Lonardo and Douglas[27]. Concerning the ground state, one observes that there is again a rather similar situation to that met in the H_2 case (Fig. 1a) in that the relative order of energies pertinent to individual formulations is the same. However, in contrast to previous findings (Figs 1a and 5a), the NH and SOM versions yield results very much alike and close to the H version.

In summary thus far, our calculations show that the tentative conclusions, concerning the properties of various AIM approaches arrived at on grounds of an analysis of a two-dimensional model calculation[8], also hold for more complex systems. It appears that one can hardly select a specific AIM version by taking a common criterion demanding the maximum closeness to the accurate (experimental or calculated) molecular energies, since this would lead to an ambiguous solution depending on the case under study. More preferably one should rule out those versions which under certain conditions fail completely to yield a physically reasonable solution — this criterion applies to the H version. The success in the quantitative correctness of the remaining (*i.e.* NH, OM, SOM) formulations is rather fortuitous, depending
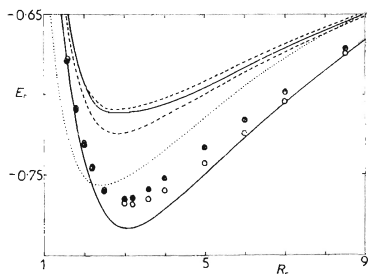

FIG. 3

Comparison of PEC's for the $^1\Sigma_u^+$ state of H_2 as obtained by various AIM formulations with both correction schemes (the highest two PEC's correspond to correction scheme 2 — the NH and SOM results practically coincide with the H ones) and *ab initio*[24] calculations (dotted)
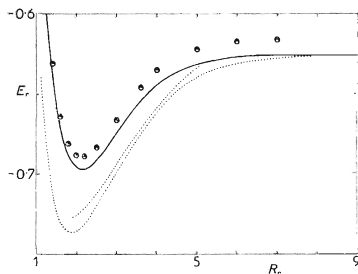
FIG. 4

Comparison of PEC's for the $^3\Sigma_g^+$ state of H_2 as obtained by various AIM formulations, *ab initio* calculations (dotted) of Gerhauser and Taylor[20] (higher curve), and Kolos and Wolniewicz[24] (lower curve)

on the subtle balance of the individual correction terms within the AIM Hamilto-
nian matrix elements. However, one can say that in most cases these versions yield
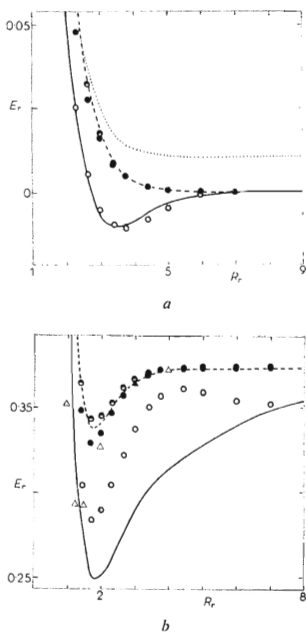correct relative positions of the PEC's, bonding character and a quite acceptable

FIG. 5

Comparison of PEC's for the two lowest
$^2\Sigma^+$ states of HeH as obtained by various
AIM formulations and *ab initio* calculations.
The zero of energy is taken to be the ex-
perimental energy of separated ground-state
atoms: -3.4037 a.u. *a)* Ground state; *ab
initio* calculation[25] (dotted) plotted in terms
of original (uncorrected) values. *b)* First
excited state; *ab initio* calculation[26] ($\triangle$)
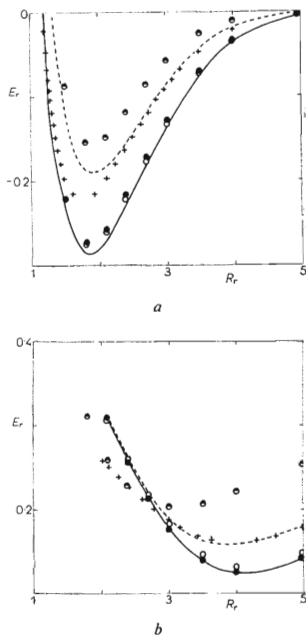corrected with regard to experimental dis-
sociation limits

FIG. 6

Comparison of the ground (*a*) and first
excited (*b*) states of $^1\Sigma^+$ for HF as ob-
tained by various AIM formulations and RKR
method[27] ($+$). The zero of energy is taken
to be the experimental energy of the separated
ground-state atoms: -100.3060 a.u.

description of the curve-crossing regions. In favour of the OM method speaks the fact that the results are relatively insensitive to those changes of the CF basis set which are connected with the use of different approximate atomic wave functions (*cf.* shift of correction schemes from type 1 to type 2 in the H_2 case). On the other hand, with the NH formulation one cannot in principle exclude the existence of complex energy values which, however, are more likely to occur with higher excited states and at extremely short internuclear distances. Ultimately it appears that the adequacy and usefulness of any AIM version depend on the quality of the approximative atomic eigenfunctions and CF basis size, and that the actual calculations should be preceded by a thorough estimation of these factors.

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