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Atoms-in-Molecules Theory: Non-Hermitian Formulation

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Non-Hermitian formulations of the ICC (Intraatomic Correlation Correction) method as well as the SAIM (Scaled Atoms-in-Molecules) theory are applied to the ground state of the hydrogen molecule. It is found that the approximation of Hermitizing the energy matrix depresses the expectation value of the energy. In the SAIM treatment, this depression is particularly large; the non-Hermitian results are in quite good agreement with experiment.

Key words: Hydrogen molecule – Atoms-in-molecules theory, non-Hermitian formulation of ~

Atoms-in-molecules (AIM) theory was formally developed by Moffitt [1] for the purpose of eliminating atomic correlation energy errors from molecular calculations. In this approach, the initial basis consists of antisymmetrized products of atomic substate eigenfunctions. Consider a diatomic molecule AB, and define the composite function

$$\Phi_i = \mathscr{A}'(\Phi_i^A \Phi_i^B). \tag{1}$$

Here, Φ_i^A is an eigenfunction for the atom A, with eigenvalue E_i^A; the subscript i signifies that this is the particular eigenstate which appears in the ith basis function Φ_i. Likewise, Φ_i^B refers to a particular eigenstate of atom B, with eigenvalue E_i^B, which appears also as a component of the composite function Φ_i. The eigenfunction Φ_i^A is antisymmetric with respect to its own N_A electrons; Φ_i^B is antisymmetric with respect to its own N_B electrons; $\mathscr{A}'$ is a partial or supplementary antisymmetrizer which causes the composite function Φ_i to be antisymmetric in all $(N_A + N_B)$ electrons.

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The Hamiltonian matrix elements can be written

$$H_{ij} = \langle \Phi_i | \mathscr{H} | \Phi_j \rangle \tag{2}$$

$$= \langle \Phi_i | \mathscr{H} \mathscr{A}' | \Phi_j^{\mathrm{A}} \Phi_j^{\mathrm{B}} \rangle \tag{3}$$

$$= \langle \Phi_i | \mathscr{A}' (\mathscr{H}_j^{\mathrm{A}} + \mathscr{H}_j^{\mathrm{B}} + \mathscr{V}_j) | \Phi_j^{\mathrm{A}} \Phi_j^{\mathrm{B}} \rangle \tag{4}$$

$$= (E_j^{\mathrm{A}} + E_j^{\mathrm{B}}) S_{ij} + V_{ij} \tag{5}$$

where

$$S_{ij} = \langle \Phi_i | \Phi_j \rangle, \tag{6}$$

$$V_{ij} = \langle \Phi_i | \mathscr{A}' \mathscr{V}_j | \Phi_j^{\mathrm{A}} \Phi_j^{\mathrm{B}} \rangle. \tag{7}$$

Equation (4) follows since the molecular electronic Hamiltonian $\mathscr{H}$ commutes with the partial antisymmetrizer $\mathscr{A}'$, and $\mathscr{H}$ can be partitioned into intraatomic and interatomic parts; this partition is determined by the assignment of electrons to the component atomic eigenfunctions Φ_i^{A} and Φ_i^{B} (the partition will differ for states of different "ionicity").

In Eq. (5), it is noted that E_j^{A} and E_j^{B} may be taken as experimental energies of the eigenstates of atoms A and B that comprise Φ_j; also, V_{ij} is an interatomic term, generally much smaller than the intraatomic contributions. Moffitt actually proposed two alternative procedures at this stage [1].

In Method I, he proposed that the S_{ij} and V_{ij} given by Eqs. (6) and (7) be obtained through the use of optimized orbital approximations to the exact atomic eigenfunctions;

$$H_{ij}^{\mathrm{I}} = (E_j^{\mathrm{A}} + E_j^{\mathrm{B}}) S_{ij}^0 + V_{ij}^0 \tag{8}$$

where the zero superscript denotes that such orbital approximations to the Φ_i^{A}, Φ_i^{B}, Φ_j^{A} and Φ_j^{B} have been utilized in evaluating those matrix elements. Such approximations yield a non-Hermitian matrix H^{I}. Since eigenvalues of such a matrix are not necessarily real, and hence may not be physically realistic, it has been customary to introduce an *additional approximation*

$$\tilde{H}^{\mathrm{I}} = \tfrac{1}{2}(H^{\mathrm{I}} + H^{\mathrm{I}+}) \tag{9}$$

where $H^{\mathrm{I}+}$ is the adjoint of H^{I}.

In developing Method II, Moffitt argued that

$$V_{ij} \sim H_{ij}^0 - (E_j^{0\mathrm{A}} + E_j^{0\mathrm{B}}) S_{ij}^0 \tag{10}$$

where *all* quantities on the right are now obtained from *ab initio* calculation, again using orbital wave functions which are optimal approximations of the atomic eigenfunctions. Incorporating Eq. (10) into Eq. (5), with $S_{ij} \sim S_{ij}^0$, we obtain

$$H_{ij}^{\mathrm{II}} = H_{ij}^0 + S_{ij}^0 (\Delta E_j^{\mathrm{A}} + \Delta E_j^{\mathrm{B}}) \tag{11}$$

where, for example,

$$\Delta E_j^{\mathrm{A}} = E_j^{\mathrm{A}} - E_j^{0\mathrm{A}} \tag{12}$$

is a correlation energy correction. Again, in order to create a Hermitian matrix, the final approximation in Moffitt's Method II is

$$\tilde{H}^{\mathrm{II}} = \tfrac{1}{2}(H^{\mathrm{II}} + H^{\mathrm{II}+}). \tag{13}$$

Note that our notation differs from that used by Moffitt.

It was recognized early that the pure atoms-in-molecules approach contained a basic deficiency [2]. For example [3], the ionic structure H^+H^-, as represented by an accurate ground state H^- eigenfunction, yields even less ionic-covalent resonance energy for H_2 than the original *ab initio* Weinbaum calculation. It was pointed out that atomic eigenfunctions must be scaled and/or deformed in order to overcome this basic deficiency [2].

Hurley suggested one approximate model, the ICC (intraatomic correlation correction) method [4], designed to account for such scaling. He argued that one should use an orbital basis *optimum for the molecule* (not for the atoms) in calculating the H and S elements in Eq. (11). Let H_{ij}^{s} and S_{ij}^{s} denote such elements computed with orbitals optimumly scaled for the molecule; it is clear that the changes $H_{ij}^{0} \to H_{ij}^{s}$ and $S_{ij}^{0} \to S_{ij}^{s}$ are significant due to interatomic effects of deformation. However, Hurley argued that correlation energy is remarkably unaffected by change of scale; thus, $\Delta E_j^{\mathrm{A}} + \Delta E_j^{\mathrm{B}}$ appearing in Eq. (11) should be calculated by the original Moffitt equation (12). Hurley's ICC model becomes

$$H_{ij}^{\mathrm{ICC}} = H_{ij}^{s} + S_{ij}^{s}(\Delta E_j^{\mathrm{A}} + \Delta E_j^{\mathrm{B}}) \tag{14}$$

Again, an approximation like Eqs. (9) or (13) was prescribed to give a final Hermitian matrix $\tilde{H}^{\mathrm{ICC}}$.

Finally, Au-ju A. Wu and the author [5] presented an exact scaled atoms-in-molecules (SAIM) theory in 1967. The basis in this theory is identical to Eq. (1) except that the atomic eigenfunctions are modified by introducing variational scaling parameters s_i^{A} and s_i^{B} into the component A-atom and B-atom eigenfunctions. Exact equations were developed for determining, by reference to experimental atomic energies, all intraatomic contributions to the energy matrix elements. All other parts of the energy matrix elements, as well as all overlap elements, are interatomic in nature, and those parts are computed using the appropriate scaled orbital wave functions. Practical implementation of this theory also led to a non-Hermitian H matrix, and an approximation like Eqs. (9) or (13) was again considered essential.

In (1969), Balint-Kurti and Karplus [6], introduced an Orthogonalized Moffitt (OM) method based upon Moffitt's second formulation, Eqs. (11–13), but utilizing Schmidt-orthogonalized composite functions. We have not included consideration of the OM method in this study.

In 1976, Tully and Truesdale [7] introduced a non-Hermitian formulation of diatomics-in-molecules (DIM) theory. As a matter of fact, AIM and DIM theories are similar in that they both require solution of the general eigenvalue-eigenvector matrix equation

$$HC = SCE. \tag{15}$$

Also, AIM and DIM theories are similar in that they both yield initially approximate non-Hermitian Hamiltonian matrices, which have generally been Hermitized, as in Eqs. (9) or (13), before being introduced into Eq. (15).

It had been observed in previous applications [8] of the DIM theory to H_3 (using two covalent plus six ionic structures) that serious instabilities occur, especially as the internuclear distances are decreased. These instabilities could not be accounted for by "over-completeness"; the instabilities could be eliminated by the rather arbitrary neglect-of-overlap approximation. However, Tully and Truesdale [7], demonstrated that the instabilities were entirely absent in the *non-Hermitian* DIM calculation.

The purpose of this paper is to report results of non-Hermitian AIM calculations on H_2. Specifically, we consider Hurley's ICC model [4] defined by Eq. (14) and the Wu-Ellison SAIM theory [5], described above. In both cases, we admit four composite functions

$$\begin{aligned}\Phi_1 &= \mathscr{A}'[1s_A(1)\alpha(1)1s_B(2)\beta(2)]\\ \Phi_2 &= \mathscr{A}'[1s_A(1)\beta(1)1s_B(2)\alpha(2)]\\ \Phi_3 &= \Phi_i^A(H^-, {}^1S)\\ \Phi_4 &= \Phi_i^B(H^-, {}^1S).\end{aligned} \tag{16}$$

For ground state H_2, symmetry requires two linear combinations, $\Phi_1 - \Phi_2$ and $\Phi_3 + \Phi_4$, which correspond in their orbital approximations to the familiar covalent and ionic structures, which in turn define the Weinbaum calculation [9].

The purpose of this paper is to report results of non-Hermitian ICC and SAIM calculations and to compare these with the conventional ones which include also the additional Hermitization approximation. In all calculations, matrix elements over orbital functions were computed with a common orbital exponent ζ, and the lowest molecular eigenvalue of Eq. (15) was minimized with respect to this orbital exponent for each internuclear distance R. In the SAIM theory [5], the scale factors $s_i^A = s_i^B = \zeta/\zeta^0$ are equal to ζ for composite functions Φ_1 and Φ_2 and equal to $\zeta/0.6875$ for composite functions Φ_3 and Φ_4[1]. Results are given in Table 1.

We also list in Table 1 the strictly *ab initio* results using the same basis in its orbital approximation, the so-called Weinbaum calculation; finally, we list results of Kolos and Wolniewicz [10], which we take as "experimental".

We see that the Hermitization approximation depresses the calculated molecular energy, just as observed in the DIM calculation on H_3. However, the complete instability obtained in the Hermitian DIM H_3 calculation [7, 8] is not obtained here in the AIM treatments of H_2.

The original SAIM results on H_2, using a Hermitian matrix, were depressingly low as is seen in Table 1. But the non-Hermitian results are in very good agreement

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[1] $\zeta^0 = 0.6875$ is the optimum $1s$-orbital exponent in the $1s^2$ approximation of H^-.

Table 1. Electronic energy of H_2 using Weinbaum function (W), ICC and SAIM theories, Hermitian (H) and non-Hermitian (NH) formulations, compared with experiment

		Electronic Energy[c]					
			ICC		SAIM		
R[a]	ζ_{opt}[b]	W	H	NH	H	NH	Expt'l[d]
0.6	1.45	0.2664	0.2474	0.2607	0.1387	0.2559	0.2304
0.8	1.37	0.0131	−0.0035	0.0037	−0.0917	−0.0109	−0.0210
1.0	1.31	−0.0937	−0.1095	−0.1046	−0.1787	−0.1249	−0.1245
1.2	1.25	−0.1362	−0.1514	−0.1477	−0.2054	−0.1691	−0.1649
1.4	1.19	−0.1477	−0.1623	−0.1594	−0.2044	−0.1794	−0.1745
1.6	1.16	−0.1440	−0.1577	−0.1553	−0.1905	−0.1728	−0.1686
1.8	1.13	−0.1325	−0.1455	−0.1433	−0.1707	−0.1580	−0.1551
2.0	1.10	−0.1177	−0.1297	−0.1278	−0.1488	−0.1397	−0.1381
3.0	1.02	−0.0467	−0.0532	−0.0524	−0.0559	−0.0543	−0.0573

[a] Internuclear distance in bohr units: 1 bohr = 5.292 nm.

[b] Optimum orbital exponent for Weinbaum (W) function.
For ICC and SAIM, same ζ appropriate for $R \geqslant 2$; larger ζ obtained as R decreases; e.g., for $R = 0.6$, $\zeta_{opt} = 1.46$, 1.47, 1.51 and 1.49 for ICC-H, ICC-NH, SAIM-H and SAIM-NH, respectively.

[c] Electronic energy including nuclear repulsion relative to H + H in hartree units: 1 hartree = 27.21 eV.

[d] Ref. [10].

with experiment. The differences with respect to the ICC model are not so pronounced.

We should add that if one were to utilize extremely accurate *ab initio* approximations to the component *atomic* eigenfunctions in a proper SAIM calculation, the H matrix would turn out to be Hermitian (or nearly so), and the final computed molecular energies would satisfy the variational principle [11]. However, when using more approximate atomic functions to evaluate interatomic contributions, it appears that the final approximation of forcing H to be Hermitian may depress significantly the lowest molecular eigenvalue. Perhaps one should omit this final approximation in all AIM calculations.

In our experience thus far with non-Hermitian formulations of AIM and DIM theories, we have yet to encounter any complex eigenvalues.

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