EFFECTS OF OUTER-SHELL ORBITALS ON THE HARTREE–FOCK ENERGIES

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The inclusion of the outer-shell orbitals such as p-orbitals on hydrogen and d-orbitals on heavier main-group atoms is treated as a perturbation on Hartree–Fock orbital energies and total energies. It is shown that the first-order effect of the basis expansion is to raise all the orbital energies. The first-order correction to the total energy is shown to vanish identically. The different behavior of the CNDO approximation is mentioned.

1. Introduction

In recent years many ab initio calculations have been published examining the roles of outer-shell orbitals (often called polarization functions such as p-orbitals on hydrogen, d- and f-orbitals on heavier atoms) in various physical and chemical properties of molecules [1–14]. Some authors [2, 3, 6, 10, 12, 13, 15] noted that when d-orbitals were included in the basis set, most of the Hartree–Fock (HF) molecular orbital (MO) energies were *raised*, although the total energy of the molecules was, of course, slightly stabilized. This effect on the orbital energies of d-orbital participation might be thought unusual from considerations based on the correlation diagram.

In the present note, the expansion of the basis set is treated as a small perturbation and it will be shown that the first-order effect of basis expansion serves to raise *all* the orbital energies. The effect on the total energy will also be discussed.

2. First-order effects of basis expansion

Let us consider two spaces composed of basis orbitals. One is called "without-χ" space and the other is called "χ" space. The sum of these two spaces is referred to as "full" space. We consider here perturbatively the expansion of the basis set used in the HF wavefunction from the without-χ space to the full space. We assume that the participation of the χ space is small enough to be treated by the perturbation theory. This assumption holds well for the participation of the outer-shell orbitals‡.

The zeroth order HF equation in the without-χ space is written as

$$F^0 | i_0 \rangle = \epsilon_i^0 | i_0 \rangle,$$

$$F^0 = h + \sum_j [-j_0 | -j_0] - [-j_0 | j_0 -], \tag{1}$$

and the HF equation for the full space is written as

$$F | i \rangle = \epsilon_i | i \rangle,$$

$$F = h + \sum_j [-j | -j] - [-j | j -], \tag{2}$$

where the spin orbitals $\{i_0\}$ and $\{i\}$ are orthonormal and the notation in the electron repulsion operator means [16]

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‡ For example, in the calculation of PF_5 [13], the fractions of the changes in the orbital energies and total energy due to the inclusion of d-orbitals are 3.2×10^{-3} (average) and 2.4×10^{-4} (see table 1).

$$\{[-i|-j] - [-i|j-]\}k(1)$$

$$= k(1)\int i^*(2)\, r_{12}^{-1}\, j(2)\, d\tau_2 - j(1)\int i^*(2)\, r_{12}^{-1}\, k(2)\, d\tau_2.$$

$F, |i\rangle$, and ϵ_i in eq. (2) are expanded perturbatively in series with respect to the order of the effect of basis expansion. In this perturbation theory, the first-order correction $|i_1\rangle$ is given as a linear combination of the χ space basis function; $|i_1\rangle = \Sigma_r d_{ir}\chi_r$. The first-order equation now becomes,

$$(F^1 - \epsilon_i^1)|i_0\rangle + (F^0 - \epsilon_i^0)|i_1\rangle = 0, \tag{3a}$$

$$F^1 = \sum_j \{[-j_1|-j_0] - [-j_1|j_0-] + [-j_0|-j_1] - [-j_0|j_1-]\}. \tag{3b}$$

The auxiliary condition coming from the orthonormality of the HF orbitals is $\langle i_0|j_1\rangle + \langle i_1|j_0\rangle = 0$. Eq. (3a) is the coupled equation for $|i_1\rangle$ and $|\epsilon_i^1\rangle$. As seen in eq. (3b), the first-order effect of the basis expansion appears only in the electron–electron repulsion part.

Multiplying eq. (3a) on the left by $\langle j_0|$ and using eq. (1), we obtain

$$\langle j_0|F^1|i_0\rangle = \langle i_0|F^1|j_0\rangle$$

$$= \epsilon_i^1\delta_{ij} + (\epsilon_i^0 - \epsilon_j^0)\langle j_0|i_1\rangle. \tag{4}$$

Especially, the first-order correction to the orbital energy becomes,

$$\epsilon_i^1 = 2\sum_j{}' \{[i_0j_1|i_0j_0] - [i_0j_1|j_0i_0]\}, \tag{5}$$

where Σ_j' means the summation except for $j = i$. For closed-shell molecules, eq. (5) is rewritten as

$$\epsilon_k^1 = 2[k_0k_1|k_0k_0]$$

$$+ 2\sum_l{}' \{2[k_0l_1|k_0l_0] - [k_0l_1|l_0k_0]\}, \tag{6}$$

where $|k\rangle$ is the kth spatial orbital.

From these equations, the sum of ϵ_i^1 is written simply as

$$\sum_i \epsilon_i^1 = -2\sum_i \langle i_0|h|i_1\rangle. \tag{7}$$

On the other hand, the first order correction to the total energy, E^1, is shown to vanish identically, i.e.,

$$E^1 = 0. \tag{8}$$

This agrees with the general rule that the Hartree–Fock energy is stable to first-order correction to the wavefunction [17].

3. Discussion

First, let us consider the effect of the outer-shell orbitals on the HF orbital energies. As a result of the fact that the first-order effect of the basis expansion appears only in the electron repulsion part [see eq. (3b)], the first-order correction to the MO energy given by eq. (5) or (6) is composed only of the electron repulsion integrals of which the Coulomb-like integrals are generally larger in magnitude than the exchange-like integrals. The signs of these Coulomb-like integrals, $[i_0j_1|i_0j_0]$ (or for closed shells, $[k_0k_1|k_0k_0]$ and $[k_0l_1|k_0l_0]$, can be seen to be positive for the important levels which mix strongly with the outer-shell orbitals. Therefore, it is concluded that the signs of all the first-order corrections, ϵ_i^1, must be positive. That is, the first-order effect of the basis expansion serves to *raise* all the orbital energies.

As to the MO's which mix strongly with the outer-shell orbitals, the actual corrections to the orbital energies are shown below to be near zero or even negative, because the first-order correction is not sifficient and the second- and higher-order corrections must be included. However, these MO's are expected to be *few* from considerations on the symmetries of the outer-shell orbitals.

This kind of behavior of the MO energies has been found in many ab initio calculations, when p-type orbitals on hydrogen and d-orbitals on 1st, 2nd, and 3rd row elements are included. To our knowledge, the following 27 molecules provide examples; H_2O [2], NH_3 [2, 18], CH_4 [2], H_2S [2, 4], SO_2 [2], SO_4^{2-} [3], thiophene [3], SF_6 [5], ClO_4^- [6], H_3PO [7], CH_3PH_2 [10], PH_3 [12, 19], PH_5 [12], PF_5 [13], C_2H_2

Table 1
Molecular orbital energies and d-orbital populations for the D_{3h} structure of PF_5 (in au)[a]

	Without d	With d	Δ[b]	q(d)[c]
$\epsilon(2e'')$	−0.681	−0.665	+0.016	
$\epsilon(6e')$	−0.702	−0.684	+0.018	
$\epsilon(5a_2'')$	−0.714	−0.695	+0.019	
$\epsilon(8a_1')$	−0.686	−0.709	−0.023	0.19
$\epsilon(1a_2')$	−0.743	−0.722	+0.021	
$\epsilon(5e')$	−0.765	−0.763	+0.002	0.09
$\epsilon(1e'')$	−0.807	−0.804	+0.003	0.08
$\epsilon(4a_2'')$	−0.870	−0.852	+0.018	
$\epsilon(4e')$	−0.877	−0.858	+0.019	
$\epsilon(7a_1')$	−1.004	−0.974	+0.030	
$\epsilon(6a_1')$	−1.650	−1.635	+0.015	0.05
$\epsilon(3a_2'')$	−1.696	−1.672	+0.024	
$\epsilon(3e')$	−1.735	−1.712	+0.023	0.03
$\epsilon(5a_1')$	−1.815	−1.782	+0.033	
$\epsilon(2a_2'')$	−5.786	−5.692	+0.094	
$\epsilon(2e')$	−5.787	−5.694	+0.093	
$\epsilon(4a_1')$	−7.883	−7.788	+0.095	
$\epsilon(3a_1')$	−26.338	−26.328	+0.010	
$\epsilon(1a_2'')$	−26.338	−26.328	+0.010	
$\epsilon(1e')$	−26.394	−26.378	+0.016	
$\epsilon(2a_1')$	−26.394	−26.378	+0.016	
$\epsilon(1a_1')$	−80.352	−80.270	+0.082	
$\sum_i 2\epsilon_i$	−515.530	−513.882	+1.648	
total energy	−837.631	−837.837	−0.205	

a) Data cited from ref. [13].
b) Changes due to the inclusion of d-orbitals on phosphorous.
c) d-orbital population on phosphorous.

[20][‡], C_2H_4 [20], C_2HF [20], C_2HCl [20], C_2H_3F [20], C_2H_3Cl [20], CH_3Cl [20], HCl [20], ClF [20], Cl_2 [20], CS [20], H_2CS [20], and NH_2PH_2 [21][‡]. An example is given in table 1 for PF_5 [13], where all but one ($8a_1'$) orbital energies are raised. As seen from the d-orbital populations shown in the last column, the d-orbitals on phosphorus mix strongly with the $8a_1'$ MO whose energy is *lowered* and moderately with the $5e'$ and $1e''$ MO's whose energies are virtually unchanged. However, some exceptions are also found in the literature. An earlier calculation of SO_4^{2-} due to Hillier et al. [4] showed that all the orbital energies were *lowered* by the indusion of d-orbitals. However, the more accurate calculation on the same molecule of Gelius et al. [3] showed the *raising* of all but two orbitals in agreement with the present result. Another example occurs for the Group IIa difluorides [14][#]. Since all of these contain significant amounts of outer p- and d-orbitals on the Group IIa atoms, the first-order result given here is not expected to provide good values. In fact, the geometry of CaF_2 was reported to depend critically upon the inclusion of d-orbitals in the calculation [14].

A note seems necessary concerning the semi-empirical calculations based on the zero-differential overlap (ZDO) approximation. The CNDO method of Santry and Segal [23] is one of the most popular methods. In eq. (5), $|j_1\rangle$ is composed only of the outer-shell orbitals and $|j_0\rangle$ is composed only of the valence-shell orbitals. Therefore, in the ZDO approximation, the first-order correction, ϵ_i^1, is actually zero. Therefore, the raising of the most of the MO's discussed above does not hold for the CNDO results and at least as many orbitals are lowered in energy as are raised [24].

As seen in eq. (8), the first-order correction to the *total* energy arising from the inclusion of the outer-shell orbitals vanishes identically. This means that although the sum of the MO energies *destabilizes* the system, the effect is exactly *cancelled* by the stabilization in the one-electron hamiltonian part. Thus, the lowering in the total energy found in the actual ab initio calculations is, as expected, due to the *second-* and *higher-order* corrections. The amounts of changes in the orbital energies (1st order) and in the total energies (2nd order) in the actual calculations serve to support this "order" relation (see footnote ‡, p. 77). It is worth pointing out that in the total energy of Ne atom, the correlation energy fraction of the contribution of d, f, g, and h orbitals is 2×10^{-4} [25], the same order of magnitude as seen in the molecular calculations (see footnote ‡, p. 77). These higher-order terms include not only the χ space but also the effect of reorganization of the MO's in the without-χ space.

Lastly, we note that the present result on the contribution of the outer-shell orbitals to the total energy

‡ The ratios of the numbers of the orbitals which are lowered by the inclusion of the d-orbitals to the total number of orbitals are as follows; C_2H_2 (1/6), C_2H_4 (3/8), C_2HF (3/9), C_2HCl (2/12), C_2H_3F (1/12), C_2H_3Cl (4/16), CH_3Cl (2/10), HCl (2/7), ClF (3/10), Cl_2 (1/13), CS (1/9), H_2CS (1/12).
‡ The ratio defined in footnote ‡ is 3/13.

Almost all the orbitals of BeF_2, MgF_2, and CaF_2 are *lowered* by the inclusion of the outer p and d orbitals on the group IIa atoms [22].

implies that the term "polarization" function, so often utilized, is actually a misnomer and should be dropped.

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References

[1] P. Millie and G. Berthier, Intern. J. Quantum Chem. 2S (1968) 67.
[2] B. Roos and P. Siegbahn, Theoret. Chim. Acta 17 (1970) 199; 21 (1971) 368.
[3] U. Gelius, B. Roos and P. Siegbahn, Theoret. Chim. Acta 23 (1971) 59; 27 (1972) 171.
[4] H. Hillier and V.R. Saunders, Intern. J. Quantum Chem. 4 (1970) 203.
[5] F.A. Gianturco, C. Guidotti, U. Lamanna and R. Moccia, Chem. Phys. Letters 10 (1971) 269.
[6] H. Johansen, Chem. Phys. Letters 11 (1971) 466.
[7] H. Marsmann, L.C.D. Groenweghe, L.J. Schaad and J.R. van Wazer, J. Am. Chem. Soc. 92 (1970) 6107.
[8] J.B. Robert, H. Marsmann, I. Absar and J.R. van Wazer, J. Am. Chem. Soc. 93 (1971) 3320.
[9] I. Absar and J.R. van Wazer, J. Phys. Chem. 75 (1971) 1360.
[10] I. Absar and J.R. van Wazer, J. Chem. Phys. 56 (1972) 1284.
[11] I. Absar and J.R. van Wazer, J. Am. Chem. Soc. 94 (1972) 2382, 6294; Theoret. Chim. Acta 29 (1973) 173.
[12] A. Rauk, L.C. Allen and K. Mislow, J. Am. Chem. Soc. 94 (1972) 3035.
[13] A. Strich and A. Veillard, J. Am. Chem. Soc. 95 (1973) 5574.
[14] J.L. Gole, A.K.Q. Siu and E.F. Hayes, J. Chem. Phys. 58 (1973) 857.
[15] J.I. Musher, J. Am. Chem. Soc. 94 (1972) 1370.
[16] A.T. Amos and J.I. Musher, Mol. Phys. 13 (1967) 509.
[17] G.G. Hall, Phil. Mag. 6 (1961) 249;
J. Goodisman and W.A. Klemperer, J. Chem. Phys. 38 (1963) 721.
[18] A. Rauk, L.C. Allen and E. Clementi, J. Chem. Phys. 52 (1970) 4133.
[19] J.M. Lehn and B. Munsch, Mol. Phys. 23 (1972) 91.
[20] J. Bloor, private communication.
[21] S. Wolfe, private communication.
[22] A. Siu, private communication.
[23] D.P. Santry and G.A. Segal, J. Chem. Phys. 47 (1967) 158.
[24] V.B. Koutecký and J.I. Musher, submitted for publication.
[25] T.L. Barr and E.R. Davidson, Phys. Rev. A1 (1970) 644.