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Broken symmetry in valence molecular region within Hartree–Fock calculations

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Symmetry restricted and unrestricted Hartree–Fock calculations at the *ab initio* LCAO–MO–SCF level have been carried out on the ground, core and valence hole states of N_2 at various N–N distances. A one-particle criterion for symmetry breaking is discussed. Strong broken-symmetry effects in the inner valence molecular region of N_2 have been found at larger N–N distances. This breaking of symmetry accompanying the symmetry unrestricted Hartree–Fock calculations of the inner valence hole states at large internuclear separations can be considered to be a common phenomenon with all highly symmetric molecules. The outer valence broken-symmetry effects with N_2 have showed some deviations as compared with these effects in the inner valence and core molecular regions.

Key words: Broken symmetry—localized hole states—N_2^+ ion

1. Introduction

Photoelectron spectroscopy [1] and, especially, the interpretation of its spectra has raised a considerable interest in quantum states of ionized molecules. Many theoretical calculations have been performed on these ionic states of molecules by various techniques among which the ΔSCF calculations [2] have taken almost monopolistic position, mainly as to the core ionized molecules. The pioneer work [3] of Bagus and Schaefer has pointed out that the *ab initio* ΔSCF calculation carried out within the symmetry restricted HF approach shows strong energy instability – as compared with the symmetry unrestricted HF result – with the core molecular ions containing several symmetry equivalent atomic sites. Furthermore, these authors have showed that the symmetry unrestricted HF calculations of core hole states lead to the localized HF result with the broken space symmetry.

In the literature [3–5] the discussion appeared whether the localized HF solution had some physical meaning. Snyder [4], employing the Slater–Zener expression for the energy of atoms, has investigated the core hole states and has suggested to think of the core hole as localized, even also in the case of molecules containing several equivalent atoms. Since the localized HF solution has provided [3] energetically better description of the core hole molecular state, it has been concluded [3] that the localized solution corresponds to a physical reality. However, Denis, Langlet and Malrieu [5] have introduced the corrected interpretation of the localized HF result and, in addition, they have stressed the fully equivalence between localized and delocalized HF solutions on the basis of CI treatment. According to their results [5], the energy difference between localized and delocalized descriptions of the core hole states disappear if we include into the CI expansion of the delocalized wave function special double excited states (valence excitation + hole change). In this way, the energy difference between both these descriptions proves to be a correlation effect. The localized description, although symmetrically incorrect, has practical advantage for being able to take into account much more relaxation energy (which includes the correlation energy from the delocalized description) at the single determinantal HF level. This problem has been studied by Cederbaum and Domcke [6] with the Green function technique as well. Their results have confirmed the correlation character of the mentioned energy instability. Ågren, Bagus and Roos have published [7] MC SCF calculations which complete the previous work [3] of Bagus and Schaefer and show instructively that the symmetry restricted HF energy overestimation can be essentially lowered by including only several double excited configurations into MC SCF wave function. Finally, there are many other papers which examine the problem from diverse aspects. Let us shortly recall some of them. As it is known the existence of degenerate or nearly degenerate states in a molecule makes a use of the adiabatic approximation questionable and, in this case, the coupling between electronic and vibrational motions becomes significant. The core hole states of highly symmetric molecules represent such a case and, therefore, they show strong non-adiabatic coupling [8] leading to the breaking of symmetry. Furthermore, the standard formal many-body theory of the core hole states has been developed [9], the projecting out of the symmetry correct wave functions from the localized ones has been studied [10], the difference between the symmetry restricted and unrestricted calculations within the X_α and HF models have been discussed [11], the use of both localized and delocalized schemes in semi-empirical calculations has been investigated [12] and criteria for the breaking of symmetry from the relaxation energy point of view has been also formulated [13].

All papers mentioned above are concerned with the core hole molecular states. As far as the valence hole states have been studied, then almost invariably in terms of valence excited states [14]. Recently several studies [15–20] have appeared which have dealt with the broken-symmetry effects in valence molecular region. These studies have indicated the direct dependence of the broken-symmetry effects on the overlap of the LCAO functions which built up the hole orbital. The change of the value of the overlap has been simulated by the change of an internuclear distance – e.g. Ag–Ag [20] or N–N [17] – so that it has been possible to investigate straightforwardly the dependence mentioned above. In this way, it has been shown [17] that the inner valence broken-symmetry effects at larger internuclear separations can attain the same intensity as the corresponding effects in the core molecular region at equilibrium geometry. This result has been confirmed independently by Benard [20] who, in addition, has succeeded to put the broken-symmetry effects in direct connection with the Čížek–Paldus doublet instability problem [21] and to formulate the existential condition for these effects. The mentioned condition reads: For an appearance of broken-symmetry effects it is necessary and sufficient if at least one negative non-filling-up root of the Čížek–Paldus doublet instability matrix [21] exists.

The goal of the present study is to discuss in more detail the results of the preliminary communication [17] and to report the symmetry restricted and unrestricted HF calculations for further N–N distances. This paper includes also investigation of the outer valence region, where some deviations have been found.

2. Computational model

For discussing changes of wave function properties caused by symmetry loosing it is satisfactory to choose a simple diatomic homonuclear molecule, e.g. N_2. Our attention will be focused on the "partner" molecular orbitals $|g\rangle$ and $|u\rangle$ which are built up of the same atomic functions $|a\rangle$, $|b\rangle$ of both symmetry equivalent N-atoms via the LCAO transformation

$$\begin{pmatrix} |1g\rangle \\ |1u\rangle \end{pmatrix} = \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ 1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix} \begin{pmatrix} |1a\rangle \\ |1b\rangle \end{pmatrix}. \tag{1}$$

The ground state closed shell wave function of a diatomic homonuclear molecule is invariant with respect to the transformation (1). By applying this transformation to the open shell hole wave function, we obtain the sum of "localized" determinants each of which describes the hole as localized either on the right symmetry equivalent atom A or on the left one B. If the symmetry is relaxed by removing those symmetry elements which cause delocalization, the transition to the localized description is made possible. Naturally, in the one-determinantal HF method the choice of one of the two localized determinants $D(A^+)$, $D(B^+)$ must be done. This choice can be controlled by the starting SCF function. Nevertheless, the loosing of symmetry does not always ensure the breaking of symmetry within HF calculations. As it has been indicated previously [15–20] the "sufficiently small" value of the atomic overlap $\langle a|b\rangle$ is one of the necessary prerequisites for such a breaking. The atomic overlap $\langle a|b\rangle$ is related to the orbital energies of molecular orbitals $|g\rangle$ and $|u\rangle$ which are built up from the atomic orbitals $|a\rangle$, $|b\rangle$ via (1). The condition of the "small" overlap $\langle a|b\rangle$ implies the "small" orbital energy splitting between states $|g\rangle$ and $|u\rangle$ (almost degeneracy) and their opening (creating hole) cuases localization in the symmetry unrestricted HF calculations. At this point it is necessary to recall the general condition reported by Malrie

[13, 22] for the breaking of symmetry which depends on the competition of the relaxation energy gain of the localized solution.

$$E_{\mathrm{SCF}}^{\mathrm{sym}}(AB)^{+} - E_{\mathrm{SCF}}^{\mathrm{unsym}}(AB^{+}) \tag{2}$$

with the resonance interaction amplitude

$$|\langle (AB^{+})|\hat{H}|(A^{+}B)\rangle| \tag{3}$$

which describes the left-right hole jumps. The condition reads [13]

$$E_{\mathrm{SCF}}^{\mathrm{sym}}(AB)^{+} - E_{\mathrm{SCF}}^{\mathrm{unsym}}(AB^{+}))\rangle|\langle (AB^{+})|\hat{H}|(A^{+}B)\rangle|. \tag{4}$$

It is possible to specify further the relaxation energy gain (2) of the fully localized solution which approaches one half [4, 6] of the total atomic relaxation energy $R(\mathrm{at})/2$ [1]. Specification of the resonance energy (3) at the one-particle level gives

$$|\langle (AB^{+})|\hat{H}|(A^{+}B)\rangle| = \langle a|\hat{F}|b\rangle = \frac{|\varepsilon_g - \varepsilon_u|}{2} \tag{5}$$

where $\hat{F}$ is the Fock operator and ε_g, ε_u stand for the orbital energies of $|g\rangle$ and $|u\rangle$ orbitals. Now the condition for the breaking of symmetry with the homonuclear diatomics can be written in terms of the one-particle criterion

$$|\varepsilon_g - \varepsilon_u| < R(\mathrm{at}) \tag{6}$$

and expressed accordingly: The breaking of symmetry of the molecular hole state, i.e. the HF instability of the doublet type, should occur if the orbital energy splitting of the partner molecular orbitals is smaller than the total atomic relaxation energy of the relevant hole in the atom. The following two relations

$$|\varepsilon_{1\sigma_g} - \varepsilon_{1\sigma_u}| \leqslant R(1s) \tag{7a}$$

$$|\varepsilon_{2\sigma_g} - \varepsilon_{2\sigma_u}| \leqslant R(2s) \tag{7b}$$

represent the one-particle criterion applied to the core and inner valence regions with homonuclear diatomics. The mentioned criteria (6), (7a), (7b) require both molecular and atomic SCF computations to be done with the same AO basis – otherwise they operate rather approximately. Accordingly, one can find [23] for the nitrogen atom the values $R(\mathrm{N}_{1s}) = 16.6$ eV, $R(\mathrm{N}_{2s}) = 3.0$ eV and $R(\mathrm{N}_{2p}) = 2.4$ eV as the approximate instability frontiers for the corresponding core and inner valence hole states of N_2.

The use of the one-particle criterion for a hole molecular orbital is well-founded when among other remaining occupied orbitals there is its orbital partner. This is evidently satisfied with N_2 for the orbitals $1\sigma_g$, $1\sigma_u$ or $2\sigma_g$, $2\sigma_u$ but not e.g. for the $3\sigma_g$ orbital because its antibonding partner $3\sigma_u$ lies high in the virtual space. In such cases the use of the one-particle criterion is not a straightforward matter.

The mentioned criterion is well fulfilled for the core MOs (7a) in contrast to the inner valence MOs (7b). That explains why in the core region the effects of broken symmetry can be so pronounced [3, 7, 10, 15–20] while in the valence region they

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[1] The relaxation contribution of the flowing molecular charge is neglected

are suppressed [15–18, 20]. Nevertheless, we still consider the cases in which a molecule is taken in its equilibrium internuclear separations. If the separations were changed, one should find at sufficiently small internuclear separations the one particle criterion non-satisfied neither for the core nor for the inner valence orbitals (the symmetry restricted HF energy overestimation should quite disappear) and, on the other hand, at sufficiently large separations the mentioned criterion should be satisfied in both the regions and thus, the symmetry restricted energy overestimation ought to be pronounced not only in the core but also in the valence regions. This is the reason why the computational model of the N_2 molecule with variable N–N distances is formulated and tested in the following sections.

3. Computational details

Ab initio LCAO–MO–SCF calculations were carried out for the ground and hole states of N_2 using the MOLALCH program package [24]. The better double-zeta basis set [25] of Gaussian functions $(9;5)/\langle 4;3\rangle$ contracted according to the scheme $\langle(6,1,1,1);(3,1,1)\rangle$ has been employed. All computations were repeated for six internuclear N–N separations, i.e. for 1.0, 1.75, 2.074 (equilibrium distance 26), 2.5, 3.0, 4.0 (a.u.). In addition, each of the computations has been performed within the two symmetry point groups – D_{2h} (symmetry restricted HF solution) and C_{2v} (symmetry unrestricted HF solution). The broken-symmetry effects within HF calculations are frequently discussed in terms of the values of ionization potentials (IPs) and for this reason we present, besides the total ground state SCF energies, the ΔSCF energy differences (IPs) obtained from the vertical approximation.

4. Results and discussion

Table 1 contains the total SCF energies of the ground states of N_2 for symmetry restricted and unrestricted HF solutions at various internuclear separations – these values of energies show that the energy stability of the ground states is conserved for all studied N–N distances.

The behavior of the orbital energies of both the HF solutions is displayed in Fig. 1 within the range 1.0–4.0 a.u. of N–N distances. The differences between the orbital energies of the ground states of symmetry restricted and unrestricted solutions were quite subtle (they differ almost on the fourth and higher decimal places – in eV). Only the $1\sigma_g$ orbital energies do not obey this rule and show the difference of several electronvolts – the corresponding orbital energy of the symmetry unrestricted HF solution (1σ MO) is drawn in Fig. 1 by the dash line.

A "small" value of the atomic overlap $\langle 1s(a)|1s(b)\rangle$ within the range N–N 1.75–4.0 a.u. results in the small orbital-energy splitting (less than 0.33 eV) of the core orbitals $1\sigma_g$, $1\sigma_u$ of N_2 (Fig. 1). Therefore, it can be expected that the symmetry unrestricted HF solution will lead to the localized solution (to the broken symmetry) in this range of internuclear separations. In such a case the

Table 1. Ground state SCF energies (a.u.) and ionization potentials (eV) of N_2 for various internuclear distances (a.u.)

	1.0		1.75		2.074	
	C_{2v}	D_{2h}	C_{2v}	D_{2h}	C_{2v}	D_{2h}
G.S.	−104.310600	−104.310600	−108.750844	−108.750844	−108.865851	−108.865851
$1\sigma_g$	429.354	429.354	410.579	418.946	411.424	420.730
$1\sigma_u$	414.717	414.717	410.579	418.566	411.424	420.606
$2\sigma_g$	36.881	36.881	42.338	42.338	39.294	39.294
$2\sigma_u$	13.608	13.608	18.348	18.348	19.983	19.983
$3\sigma_g$	13.038	14.105	16.334	16.334	15.843	15.843

	2.5		3.0		4.0	
	C_{2v}	D_{2h}	C_{2v}	D_{2h}	C_{2v}	D_{2h}
G.S.	−108.757312	−108.757312	−108.562067	−108.562067	−108.253755	−108.253755
$1\sigma_g$	412.129	422.517	412.023	423.668	405.804	424.312
$1\sigma_u$	412.129	422.471	412.023	423.647	405.804	424.306
$2\sigma_g$	35.390	35.390	32.020	32.020	18.847	28.739
$2\sigma_u$	21.880	21.880	23.705	23.705	18.847	25.786
$3\sigma_g$	15.106	15.106	13.990	13.990	11.779	11.779

ionization potentials of the $1\sigma_g$ and $1\sigma_u$ orbitals obtained within the C_{2v} symmetry should have mutually the same values and, at the same time, these values should be substantially smaller than the delocalized IPs within the D_{2h} symmetry. The corresponding values in Table 1 (and their differences in Table 2) confirm that behavior (the one-particle criterion (7a) is fulfilled within this range of internuclear separations). If the shortening of the internuclear distance N–N continue (N–N < 1.75 a.u.), the atomic overlap and also the orbital-energy splitting enlarge their values; at the separation 1.0 a.u. the orbital-energy splitting attains the value 14.45 eV. This large splitting does not permit the symmetry unrestricted HF calculation to result in the localized solution. If it is the case, IPs of the core MOs cannot differ between the symmetries C_{2v} and D_{2h} – the symmetry unrestricted C_{2v} calculation will lead to the delocalized D_{2h} solution (breaking of symmetry does not occur). The corresponding numerical values in Table 1 and 2 satisfy these expectations (the 2 eV difference between our value 14.45 eV of the instability

Table 2. Differences between symmetry restricted and unrestricted IPs (eV) – correlation corrections

N–N (a.u.)	1.0	1.75	2.074	2.5	3.0	4.0
$1\sigma_g$	0	8.367	9.306	10.388	11.645	18.508
$1\sigma_u$	0	7.987	9.182	10.342	11.624	18.502
$2\sigma_g$	0	0	0	0	0	9.892
$2\sigma_u$	0	0	0	0	0	6.939
$3\sigma_g$	1.067	0	0	0	0	0

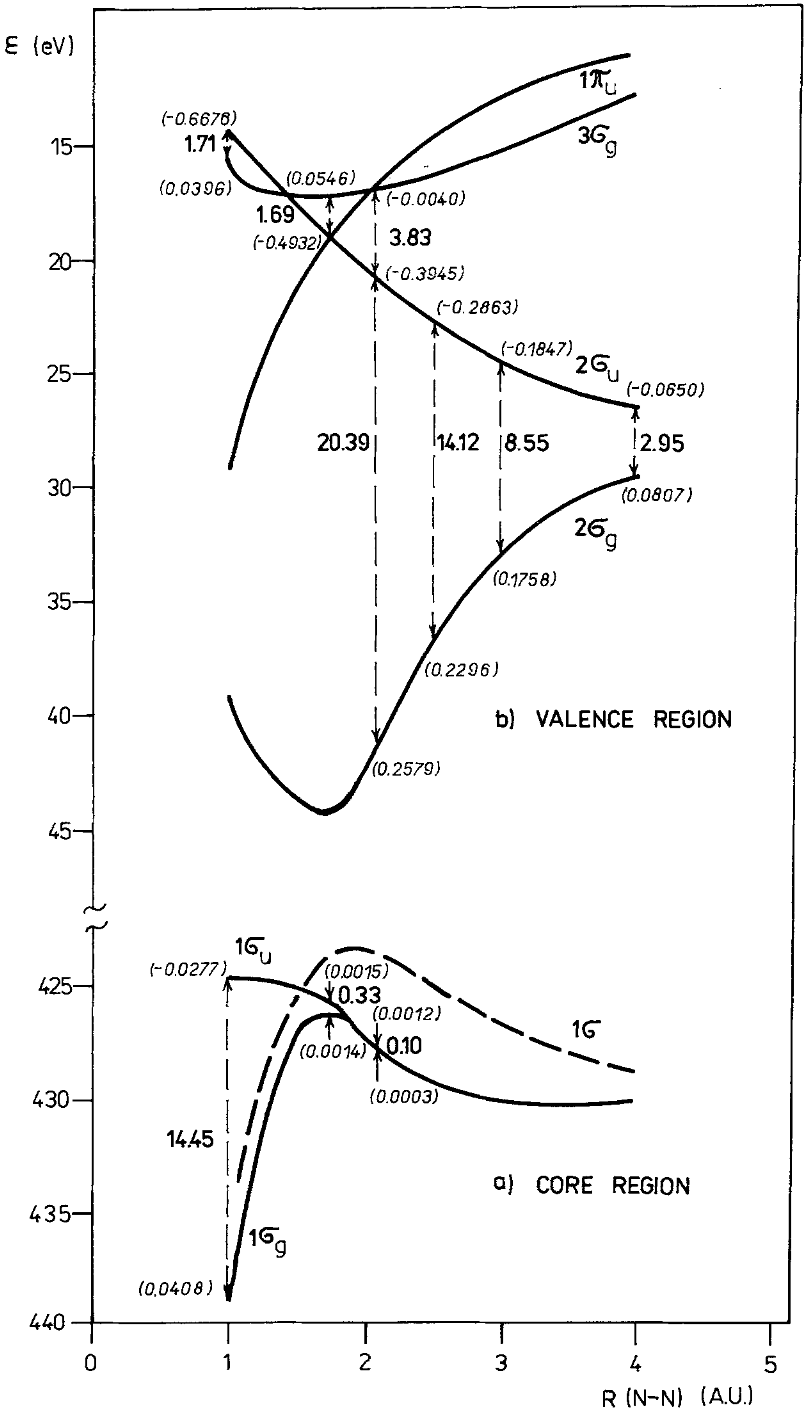

Fig. 1. Correlation diagram of orbital energies ε for $N_2(1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u, 3\sigma_g, 1\pi_u)$. The numerical values in parantheses are *s*-components of Mulliken overlap analysis

frontier (7a) and the value of the relevant atomic relaxation energy $R(N_{1s})=16.6$ eV [23] is undoubtedly connected to the inconsistent AO bases used in either computations). Hence the symmetry restricted HF energy overestimations will disappear at short internuclear distances ($\lesssim 1.0$ a.u.) while at larger distances (>1.0 a.u.) they will resist. Benard [20] has come to the analogous result with the Ag–Ag model.

Fig. 1 also shows the behavior of the valence orbital energies of the $2\sigma_g$, $2\sigma_u$, $3\sigma_g$ and $1\pi_u$ orbitals of N_2. We are interested in the inner valence ($2\sigma_u$, $2\sigma_g$) and partly in outer valence ($3\sigma_g$) regions. First, let us discuss the inner valence region. From comparing the orbital-energy splittings between the core MOs (0.1 eV) and inner valence MOs (20.39 eV) at the equilibrium N–N distance (2.074 a.u.) it is directly seen why the inner valence broken-symmetry effects are suppressed and why the ΔSCF technique in spite of relaxed symmetry is not successful in describing the inner valence hole states at internuclear distances near the equilibrium. Naturally, the energy splitting 20.39 eV is too large (see criterion (7b)) for the localization of the inner valence hole in contrast to the 0.1 eV splitting in the core region where the full hole localization occurs. The considerable splitting of the inner valence orbitals also remains at larger N–N distances (>2.074 a.u.) so that localization cannot take place (Tables 1, 2). At the separation 4.0 a.u. the splitting decreases to the value 2.95 eV (Fig. 1) and the symmetry unrestricted C_{2v} calculations result in the localized solution (the criterion (7b) is satisfied and the broken symmetry occurs). The respective inner valence IPs (Table 1) and their differences (Table 2) show the typical features of the localized solution. This fact is partly supported by the results presented in the work of Nesbet [27], who has studied the wave function of the ground state of N_2 at various N–N distances and has also found the distance 4.0 a.u. to be the characteristic one for changing delocalized valence MOs to localized atomic orbitals. So that the pronounced inner valence broken-symmetry effects with N_2 appear at rather large internuclear distances (4.0 a.u.). Benard reported [20] analogous result with the Ag–Ag system.

As to the outer valence $3\sigma_g$ MO, the situation is rather different. From Tables 1, 2 it is apparent that the breaking of symmetry does not occur at larger separation but, on the contrary, at the shorter one (1.0 a.u.). That fact must be connected with the behavior of the valence orbital-energy curves similarly as in the foregoing cases. In accordance with the one-particle criterion, the interaction of the $3\sigma_g$ MO with its antibonding partner $3\sigma_u$ should be crucial. Since the $3\sigma_u$ orbital is non-occupied and lies in the virtual space, the mentioned interaction loses its significance. At larger separations the highest occupied $1\pi_u$ orbital is the nearest one to $3\sigma_g$ but, from the view of the one-particle criterion, $1\pi_u$ is inconvenient for the interaction with $3\sigma_g$. At shorter separations the $3\sigma_g$ MO approaches the $2\sigma_u$ MO which can be employed for interaction leading to the breaking of symmetry. However, it has a smaller total quantum number by one as compared with $3\sigma_g$. Although among the studied N–N distances there are two cases (1.0 and 1.75 a.u.) at which the orbitals $2\sigma_u$ and $3\sigma_g$ have relatively small orbital-energy splitting (1.7 eV), the breaking of symmetry appears only at one of them (1.0 a.u.).

The respective 1 eV lowering of the HF energy (full localization does not occur but MOs are polarized) is much less in comparison with the foregoing cases of the broken symmetry. That might be related to the fact that the interaction between $3\sigma_g$ and $2\sigma_u$ is realized by the atomic orbital components which possess mutually different characters of localization. At the distance 1.75 a.u. the $2\sigma_u$ orbital-energy curve is crossed by the $1\pi_u$ curve and the quasidegenerate one-particle state $(2\sigma_u, 1\pi_u)$ appears in which the $1\pi_u$ component may perturb the interaction with the $3\sigma_g$ MO and thus, the breaking of symmetry does not occur.

Let us concentrate on correlation effects. In the introductory section the correlation character of the symmetry restricted HF energy overestimation has been mentioned. The differences of IPs between delocalized ($\mathrm{IP}_g^0 \neq \mathrm{IP}_u^0$) and localized ($\mathrm{IP}_a = \mathrm{IP}_b$) HF solutions stand for correlation corrections (c_g, c_u)

$$c_g = \mathrm{IP}_a - \mathrm{IP}_g^0, \qquad c_u = \mathrm{IP}_b - \mathrm{IP}_u^0. \tag{8}$$

Table 2 includes the values of correlation corrections for N_2, which confirm some expected facts: when the inner valence orbital-energy splitting approach a sufficiently small value (e.g.. ~3 eV for N–N = 4.0 a.u., Fig. 1), the correlation effects will attain approximately the same intensity as they achieve in the core region at equilibrium separation. In addition, from Eqs. (8) the relation between the localized and delocalized IPs can be determined

$$\mathrm{IP}_a = \mathrm{IP}_b = (\mathrm{IP}_g + \mathrm{IP}_u)/2, \tag{9}$$

where the delocalized potentials (IP_g, IP_u) contain the correlation corrections ($\mathrm{IP}_g = \mathrm{IP}_g^0 + c_g$, $\mathrm{IP}_u = \mathrm{IP}_u^0 + c_u$). Under zero overlap condition (full localization), Eq. (9) could be correlated directly with the similar relationship derived by Cederbaum and Domcke [6].

In the SCF computations of potential curves of hole molecular states the meaning of the studied correlation corrections for various internuclear distances is well established. In such cases it would be worthwhile to know in which intervals of internuclear distances the correlation corrections will play a major or minor role. From Table 2 it is apparent that the $3\sigma_g$ other valence hole state correlation effects with N_2 are more significant at shorter N–N distances (1.0 a.u.). However, this need not be the case for other molecules containing symmetry equivalent atoms, since their outer valence orbital configurations (e.g. orbital-energy splitting and behavior of orbital-energy curves at various internuclear distances) may not be the same as in N_2. On the other hand, the inner valence regions of molecules contain practically always the groups of MOs which possess the proper symmetry properties allowing the breaking of symmetry. For this reason it can be expected that the inner valence correlation effects similar to those of N_2 will also appear in many other molecules having several symmetry equivalent sites. The strong inner valence hole state correlation effects will occur especially at large internuclear distances of these highly symmetric molecules. This fact is not surprising because it is widely known that the SCF potential energy curves are overestimated at large internuclear distances as a consequence of a non-included electron correlation. Broken-symmetry effects based on the hole localization have made possible an uncommon view of this energy overestimation with the valence hole states of highly symmetric molecules.

4. Conclusions

The symmetry restricted and unrestricted HF calculations performed on N_2^+ have shown that the sequence of the N–N distances can be divided into three regions. In the first region (N–N $<$ 1.0 a.u.) the one-particle criterion is not satisfied for both the core and inner valence MOs and hence the HF hole instabilities fully disappear for the core and inner valence ionic states. In the second region (1.0–4.0 a.u.) the orbital-energy splitting considerably decreases especially for the core orbitals (0.33 eV) so that the "opening" of these orbitals, in contrast to the inner valence ones, will lead to the breaking of symmetry in the corresponding HF calculations. In the third region (N–N $\gtrsim$ 4.0 a.u.) the inner valence orbital-energy splitting achieves the sufficiently small values as well ($\sim$3 eV) and, therefore, the breaking of symmetry takes place also with the inner valence orbitals.

The outer valence orbitals show formally different behavior. Since their antibonding partners are actually not always present among other occupied MOs, the interactions with the proper inner valence partners (if they exist) are most important from the broken-symmetry point of view. The interaction of such groups of orbitals, however, leads to the weaker broken-symmetry effects because they contain diversely localized atomic components.

Furthermore, the present computations have shown the one-particle criterion to be a useful tool for estimation of the broken-symmetry effects, appearing within the symmetry unrestricted HF calculations. From all studied cases the largest orbital-energy splitting which admitted the broken symmetry had the value of $\sim$3 eV.

It has been confirmed that the effects of the broken symmetry can be relevant not only for the core region of molecules, where they have been largely studied, but also for the valence molecular region. The inner valence hole states of N_2 give evidence of it because for the distance N–N = 4.0 a.u. the studied inner valence effects have been of the same magnitude as those in the core region at equilibrium separation. These pronounced core and inner valence effects fully disappear at small internuclear distances (N–N $\lesssim$ 1.0 a.u.).

The broken symmetry effects seem to be important when the SCF potential curves of the ionized molecules which contain several symmetry equivalent sites are to be calculated. The SCF calculations within the broken-symmetry approach enable especially at larger internuclear distances to include the considerable part of correlation energy in both the core and inner valence regions. Unfortunately, this approach introduces a discontinuity on the curve of potential energy (in the first point of the breaking of symmetry) and may be connected with the greater numerical difficulties as compared with the symmetry restricted SCF calculations. Nevertheless, in comparison with the extensive CI treatment, the symmetry unrestriced HF approach is numerically more advantageous.

Finally, it is possible to mention that the effects of broken symmetry appear as a consequence of an "inappropriateness" of the single determinantal description of electron systems. At the same time, those effects also possess useful features, namely, the possibility to include a large part of correlation energy. The present study has confirmed that those useful features are not only restricted to the core hole states but that they can also occur in the same intensive form with the inner valence hole states of highly symmetric molecules.

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