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Delocalized and Localized Pictures of Excited and Ionized States

II. Polarization of the Valence Shell under a Core Ionization

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The valence shell repolarization under a core ionization in a diatomic molecule as N_2 is analyzed through localized and delocalized pictures, showing their total equivalence. The interpretation is easier in the localized model, appearing mainly through local single excitation processes; in the delocalized model the repolarization effect is hidden (partly or totally) under double excitation processes involving simultaneous excitations in the valence shell and hole change in the core level, appearing therefore as a "correlation effect". This effect is analyzed for n Be atoms, showing a n^{-1} behaviour of the single excitations effect in the delocalized model, and explains the Hartree-Fock unstability numerically verified on O_2^+, but it prevents to give any physical meaning to the "localization of the core hole in a diatomic molecule".

Key words: Localized orbitals – Excited states – Valence shell polarization – Positive ions

1. Introduction

The photoelectron spectroscopy allows us to study the highly excited ionized states of atoms and molecules [1], for instance the levels corresponding to an ejection of one "electron"[1] from the 1*s* levels of diatomic molecules, such as the oxygen molecule [2]. In such an ionized excited state, the valence "electrons" are in a strongly modified field and their distribution should be reorganized through a polarization effect of the change in the core field. The present paper deals with an analysis of the phenomenon on both delocalized and localized descriptions of the ionized state, showing the deep agreement of the two descriptions under their apparent divergence.

These ionized excited states have already received some considerations from the theoreticians. Snyder first claimed that the polarization of the valence shell was stronger if the 1*s* core was localized on one of the atoms of a diatomic such as N_2, and that this phenomenon led to a physical localization of the 1*s* core [4].

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[1] The concepts of core electrons or valence electrons in general refer to the shell model of the molecule, i.e. to the independant particle approximation. This is the reason why we speak of core or valence "electrons", specifying their quasi-particle nature. Loge theory (3), i.e. the consideration of the distribution of electrons in the physical space R^3, sometimes allows rigorous considerations upon the physical electrons.

Bagus and Schaeffer [5] later on, performed an unrestricted Hartree-Fock calculation on the 1*s* ionized state of the O_2 molecule where they allowed a breaking of the symmetry of the molecular orbitals; the unsymmetrical HF solution where the 1*s* core is localized on one of the nuclei is lower in energy than the symmetrical HF solution, and these authors concluded that their "calculation shows that the 1*s* hole states of O_2^+ are localized, that is the ejected electron has been specifically moved from one of the two atoms". The present discussion shows that the localized or delocalized nature of the 1*s* hole is not correctly analyzed and that the Hartree-Fock unstability with respect to the symmetry constraint is irrelevant to answer such a problem.

For the sake of simplicity the discussion will first consider the case of the N_2 molecule instead of O_2; the closed shell nature of the ground state wave function greatly simplifies the notations.

2. Delocalized and Localized Description of an Ionized System

The ionized states may be considered as a special class of excited states: referring to the shell model of the excitation (promotion of an electron from a discrete level in the Fermi sea, towards a discrete level above the Fermi sea) one may consider the ionization as an excitation towards a virtual molecular orbital removed to infinity from the molecule, having no matrix element with any molecular orbital of the molecule. This introduction of a fictitious MO at infinity in general would be of no practical use, but from a conceptual point of view this remark shows that all the methods and conclusions obtained for excited states are relevant for the ionized states as well.

For the excited states it is well known that two rather different descriptions have been proposed. The usual, dominant description uses symmetry MO's, which are obtained from a more or less sophisticated procedure (going from a direct diagonalization of a topological hamiltonian as in the Hückel method to the variational calculation of the MO's for the specific excited state). This description exhibits a single determinantal description of the excited state which possesses at least the correct symmetry properties, and sometimes sufficient physical realism to be considered as a satisfying zeroth order description of the excited state, analogous to the closed shell HF determinant for the ground state. An other possible description starts from localized MO's for instance from the localized MO's which are unitary transforms of the delocalized, symmetry adapted, canonical HF MO's. Both sets of MO's are equivalent for the ground state; for the excited states, the determinants corresponding to local "excitations" (promotion of one "electron" from a localized MO under the Fermi level to a virtual (localized) MO are not symmetry adapted, and may be (nearly) degenerate in energy. The construction of a reasonable symmetry adapted description of the excited state requires us to consider a proper combination of localized "excitations", i.e. of locally excited determinants. For instance this combination may result from the diagonalization of the configuration interaction (CI) matrix restricted to a class of such singly excited determinants [6], or of all singly excited determinants [7]. These are the so called "excitonic" methods, frequently used in solid state physics but less popular in molecular physics.

The two approaches may be translated immediately for ionic problems. The first one corresponds to the usual description of the ion, the second one might be called the "excitonic" method. This method in some sense already exists. After the discovery of the equivalence of delocalized and localized MO's for the ground state [8], various authors [9] applied the idea of transferability of the localized MO's from one bond to another, or from one molecule to another, to build the Fock operator between the localized MO's and to study the positive ions of the molecule by diagonalizing it. This procedure is exactly equivalent to the CI between the singly excited states for the case where the virtual MO is remoted to infinity; all the singly excited determinants ($p \rightarrow \infty$) interact, through the matrix element $-\langle p|\mathscr{F}|q\rangle$ if p, q and $\mathscr{F}$ refer to the ground state HF solution. The "excitonic" procedure generally stops at this level, as well as the excitonic method, but it is possible to go further towards the exact solution by improving the CI using either the delocalized or the localized sets of MO's. The first case represents the usual CI approach of the excited state, introducing singly, doubly and triply excited determinants, for instance in a perturbative scheme [10]; the other approach may be called the generalized "excitonic" method [11], and the purpose of this series of papers [12] is to make the comparison between them for the case of open shell ions.

2.1. *Definition of the* MO's *of the* N_2 *molecule*

For this test case originally discussed by Snyder [4], we may consider the ground state (HF) wave function

$$\Phi_0^0 = |\varphi_s \bar{\varphi}_s \varphi_a \bar{\varphi}_a \sigma \bar{\sigma} \pi \bar{\pi} \underline{\pi} \bar{\underline{\pi}} n_1 \bar{n}_1 n_2 \bar{n}_2| , \tag{1}$$

where the σ, π, and $\underline{\pi}$ MO's are the three bond MO's, n_1 and n_2 are localized σ lone pairs on each atom and where φ_s and φ_a are the symmetry adapted $1s$ levels

$$\varphi_s = 1/\sqrt{2}(\phi_1 + \phi_2) \qquad \varphi_a = 1/\sqrt{2}(\phi_1 - \phi_2) \tag{2}$$

ϕ_1 and ϕ_2 being $1s$ localized MO's. The consideration of localized lone pairs is arbitrary and does not play a significant role at the present level. An equivalent description is:

$$\phi_0^0 = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 \sigma \bar{\sigma} \pi \bar{\pi} \underline{\pi} \bar{\underline{\pi}} n_1 \bar{n}_1 n_2 \bar{n}_2| , \tag{3}$$

where the $1s$ MO's are localized. The two diagonal terms of the Fock operator relative to ϕ_1 and ϕ_2 are equal

$$\langle \phi_1|\mathscr{F}|\phi_1\rangle = \langle \phi_2|\mathscr{F}|\phi_2\rangle \tag{4}$$

and their non-diagonal matrix element is very small, due to the strong spatial localization of the cores, leading to an almost zero differential overlap

$$\phi_1(r)\,\phi_2(r) \simeq 0\,\forall r\,, \qquad \langle \phi_1|\mathscr{F}|\phi_2\rangle = \varepsilon\,. \tag{5}$$

One may notice that $\langle\varphi_s|\mathscr{F}|\varphi_s\rangle-\langle\varphi_a|\mathscr{F}|\varphi_a\rangle=2\varepsilon$. The delocalized symmetrical and antisymmetrical 1*s* levels are almost degenerate and so are therefore the two symmetry adapted ionized states descriptions (for $S_3=-1/2$ doublets).

$$\begin{aligned}\psi^+_{\varphi_s}(0)&=a_{\varphi_s}\phi_0^0=|\bar{\varphi}_s\varphi_a\bar{\varphi}_a\sigma\bar{\sigma}\,\ldots\,n_2\bar{n}_2|\\ \psi^+_{\varphi a}(0)&=a_{\varphi_a}\phi_0^0\quad|\varphi_s\bar{\varphi}_s\bar{\varphi}_a\sigma\bar{\sigma}\,\ldots\,n_2\bar{n}_2|,\end{aligned}\tag{6}$$

where a_{φ_i} is an annihilator of the MO φ_i. If one considers the two determinants corresponding to localized ionizations

$$\begin{aligned}\psi^+_{\phi_1}&=a_{\phi_1}\phi_0^0=|\bar{\phi}_1\phi_2\bar{\phi}_2\sigma\bar{\sigma}\,\ldots\,n_2\bar{n}_2|\\ \psi^+_{\phi_2}&=a_{\phi_2}\phi_0^0=|\phi_1\bar{\phi}_1\bar{\phi}_2\sigma\bar{\sigma}\,\ldots\,n_2\bar{n}_2|,\end{aligned}\tag{7}$$

and

these two determinants are degenerate

$$\begin{aligned}&\langle\psi^+_{\phi_1}|\mathscr{H}|\psi^+_{\phi_1}\rangle=\langle\psi^+_{\phi_2}|\mathscr{H}|\psi^+_{\phi_2}\rangle=\langle\phi_0^0|\mathscr{H}|\phi_0^0\rangle-\langle\phi_1|\mathscr{F}|\phi_1\rangle\\ &\langle\psi^+_{\phi_1}|\mathscr{H}|\psi^+_{\phi_2}\rangle=-\varepsilon\end{aligned}\tag{8}$$

and

$$\begin{aligned}\langle\psi^+_{\varphi_s}|\mathscr{H}|\psi^+_{\varphi_s}\rangle&=\langle\phi_0^0|\mathscr{H}|\phi_0^0\rangle-\langle\phi_1|\mathscr{F}|\phi_1\rangle-\varepsilon\\ \langle\psi^+_{\varphi_a}|\mathscr{H}|\psi^+_{\varphi_a}\rangle&=\langle\phi_0^0|\mathscr{H}|\phi_0^0\rangle-\langle\phi_2|\mathscr{F}|\phi_2\rangle+\varepsilon.\end{aligned}\tag{9}$$

In the excitonic description of the ion, the zeroth order wave function is a linear combinations of (two) determinants

$$\psi^+_{\varphi_s}=1/\sqrt{2}(\psi^+_{\phi_1}+\psi^+_{\phi_2}),\qquad\psi^+_{\varphi_a}=1/\sqrt{2}(\psi^+_{\phi_1}-\psi^+_{\phi_2})\tag{10}$$

which actually may be written in the form of a single determinant. This is a drastic difference between the ionization and the excitation processes; in the localized description the CI of single excitations leads to a linear combination of determinants equivalent to the Koopmans' theorem single determinant for the ion, while it leads to a multiconfigurational description richer than the virtual orbital approximation for the excited state. Despite this equivalence we shall go on with the two determinants localized description to perform the further CI.

3. The Intra-Valence Excitations

Within the valence shell, one may consider the $\sigma\to\sigma^*$, and $\pi\to\pi^*$ single excitations. These single excitations will not lead to any energetic change for the ground state even if ϕ_0^0 is not self consistent, since the $\sigma\sigma^*$ or $\pi\pi^*$ excited determinants are antisymmetric with respect to the center of symmetry of the diatomic molecule,

$$\langle\phi_0^0|\mathscr{H}|a^+_{\sigma^*}a_\sigma\phi_0^0\rangle=\langle\phi_0^0|\mathscr{H}|a^+_{\pi^*}a_\pi\phi_0^0\rangle=0.\tag{11}$$

The same excitations are possible upon the ion. If we first consider the symmetric ion ($\psi^+_{\varphi_s}$). The same symmetry considerations are valid, and

$$\langle\psi^+_{\varphi_s}|\mathscr{H}|a^+_{\sigma^*}a_\sigma\psi^+_{\varphi_s}\rangle=\langle\psi^+_{\varphi_s}|\mathscr{H}|a_{\pi^*}a_\pi\psi^+_{\varphi_s}\rangle=0.\tag{12}$$

In the delocalized scheme the single excitations $\sigma\to\sigma^*$, or $\pi\to\pi^*$ do not lead to an energy stabilisation of the positive symmetrical ion.

Let us turn now to the excitonic description. The $\sigma\sigma^*$ excitation leads to *two* types of determinants $a^+_{\sigma^*}a_\sigma\psi^+_{\phi_1}$ and $a^+_{\sigma^*}a_\sigma\psi^+_{\phi_2}$ (and the β spin analogous). Let us consider their interaction with $\psi^+_{\phi_1}$ and $\psi^+_{\phi_2}$.

$$\begin{aligned}\langle a^+_{\sigma^*}a_\sigma\psi^+_{\phi_1}|\mathscr{H}|\psi^+_{\phi_1}\rangle &= \langle\sigma^*|\mathscr{F}-\mathscr{J}_{\phi_1}+\mathscr{K}_{\phi_1}|\sigma\rangle \\ \langle a^+_{\bar{\sigma}^*}a_{\bar{\sigma}}\psi^+_{\phi_1}|\mathscr{H}|\psi^+_{\phi_1}\rangle &= \langle\sigma^*|\mathscr{F}-\mathscr{J}_{\phi_1}|\sigma\rangle\,,\end{aligned} \tag{13}$$

where $\mathscr{F}$ is the ground state Fock operator, $\mathscr{J}_{\phi_1}$ and $\mathscr{K}_{\phi_1}$ the Coulomb and exchange operators relative to the MO ϕ_1,

$$\begin{aligned}\langle a^+_{\sigma^*}a_\sigma\psi^+_{\phi_1}|\mathscr{H}|\psi^+_{\phi_2}\rangle &= \langle\bar{\phi}_1\phi_2\bar{\phi}_2\sigma^*\bar{\sigma}\ldots n_2\bar{n}_2|\mathscr{H}|\phi_1\bar{\phi}_1\bar{\phi}_2\sigma\bar{\sigma}\ldots n_2\bar{n}_2\rangle \\ &= -\langle\bar{\phi}_1\phi_2\bar{\phi}_2\sigma^*\bar{\sigma}\ldots n_2\bar{n}_2|\mathscr{H}|\bar{\phi}_1\phi_1\bar{\phi}_2\sigma\bar{\sigma}\ldots n_2\bar{n}_2\rangle \\ &= -\langle\sigma^*\phi_2|\sigma\phi_1\rangle+\langle\sigma^*\phi_2|\phi_1\sigma\rangle \\ \langle a^+_{\bar{\sigma}^*}a_{\bar{\sigma}}\psi^+_{\phi_1}|\mathscr{H}|\psi^+_{\phi_2}\rangle &= -\langle\sigma^*\phi_2|\sigma\phi_1\rangle\,.\end{aligned} \tag{14}$$

The final matrix elements

$$\begin{aligned}\langle a^+_{\sigma^*}a_\sigma\psi^+_{\phi_1}|\mathscr{H}|\psi^+_{\varphi_s}\rangle &= \frac{1}{\sqrt{2}}[\langle\sigma^*|\mathscr{F}-\mathscr{J}_{\phi_1}+\mathscr{K}_{\phi_1}|\sigma\rangle-\langle\sigma^*\phi_2|\sigma\phi_1\rangle+\langle\sigma^*\phi_2|\phi_1\sigma\rangle] \\ \langle a^+_{\bar{\sigma}^*}a_{\bar{\sigma}}\psi_{\phi_1}|\mathscr{H}|\psi_{\varphi_s}\rangle &= \frac{1}{\sqrt{2}}[\langle\sigma^*|\mathscr{F}-\mathscr{J}_{\phi_1}|\sigma\rangle-\langle\sigma^*\phi_2|\sigma\phi_1\rangle]\end{aligned} \tag{15}$$

are different from zero. One may notice that $\langle\sigma^*|\mathscr{F}|\sigma\rangle=0$, the $\phi_1\phi_2$ distribution is negligible and the $\sigma\phi$ or $\sigma^*\phi$ distributions lead to some exchange type integrals which are small in comparison with $\langle\sigma^*|\mathscr{J}_{\phi_1}|\sigma\rangle$, representing the electrostatic interaction between the core electronic charge $(\phi_1)^2$ and the transition dipole $\sigma\sigma^*$;

$$\begin{aligned}&\langle a^+_{\sigma^*}a_\sigma\psi^+_{\phi_1}|\mathscr{H}|\psi^+_{\varphi_s}\rangle=\langle a^+_{\sigma^*}a_\sigma\psi^+_{\phi_2}|\mathscr{H}|\psi^+_{\varphi_s}\rangle \\ &\simeq\langle a^+_{\bar{\sigma}^*}a_{\bar{\sigma}}\psi^+_{\phi_1}|\mathscr{H}|\psi^+_{\varphi_s}\rangle\equiv\langle a^+_{\bar{\sigma}^*}a_{\bar{\sigma}}\psi^+_{\phi_2}|\mathscr{H}|\psi^+_{\varphi_s}\rangle\simeq-\langle\sigma^*|\mathscr{J}_{\phi_1}|\sigma\rangle/\sqrt{2}\,.\end{aligned} \tag{16}$$

The energetic effect of these interactions may be calculated through second order perturbation theory. The second order correction due to the $\sigma\sigma^*$ excitations is given by

$$\varepsilon^2_{\sigma\sigma^*}=\frac{2\langle\sigma^*|\mathscr{J}_{\phi_1}|\sigma\rangle^2}{\Delta E\begin{pmatrix}\sigma^*\\ \sigma\end{pmatrix}}\,, \tag{17}$$

where $-\Delta E\begin{pmatrix}\sigma^*\\ \sigma\end{pmatrix}$ is the excitation energy associated with the $\sigma\to\sigma^*$ excitation process [13] $\left(\text{for instance in the Moller-Plesset [14] definition of the imperturbed hamiltonian } \Delta E\begin{pmatrix}\sigma^*\\ \sigma\end{pmatrix}=\langle\sigma^*|\mathscr{F}|\sigma^*\rangle-\langle\sigma|\mathscr{F}|\sigma\rangle\right)$. The factor 2 results from the consideration of the four determinants. Therefore the same single excitations $\sigma\sigma^*$ (or $\pi\pi^*$) which did not have any effect on the symmetrical ion in the delocalized model, lead to a significant energy lowering in the excitonic model.

What is the status of this apparent divergence between the delocalized and the localized models? In principle the exact solution is obtainable in both representations since they represent the same CI in the same space, the only difference concerning the basis sets. Therefore the correction appearing in the excitonic treatment should appear elsewhere in the delocalized model or cancel with another term. The present paragraph shows that the excitonic $\varepsilon^2_{\sigma\sigma^*}$ correction is not an artifact and actually elsewhere appears in the delocalized model. Let us consider the delocalized determinant

$$a^+_{\sigma^*} a_\sigma \psi^+_{\varphi_a} = a^+_{\sigma^*} a_\sigma a^+_{\varphi_s} a_{\varphi_a} \psi^+_{\varphi_s} = a^+_{\sigma^*} a_\sigma a_{\varphi_a} \phi^0_0 \tag{18}$$

and its β spin conterpart $(a^+_{\bar{\sigma}^*} a_{\bar{\sigma}} \ldots)$. These determinants are doubly excited with respect to the zeroth order description of the state $\psi^+_{\varphi_s}$ but they interact with it:

$$\begin{aligned}\langle a^+_{\sigma^*} a_\sigma \psi^+_{\varphi_a} | \mathscr{H} | \psi^+_{\varphi_s} \rangle &= \langle \varphi_s \bar{\varphi}_s \bar{\varphi}_a \sigma^* \bar{\sigma} \ldots n_2 \bar{n}_2 | \mathscr{H} | \bar{\varphi}_s \varphi_a \bar{\varphi}_a \sigma \bar{\sigma} \ldots n_2 \bar{n}_2 \rangle \\ &= -\langle \varphi_s \bar{\varphi}_s \bar{\varphi}_a \sigma^* \bar{\sigma} \ldots n_2 \bar{n}_2 | \mathscr{H} | \varphi_a \bar{\varphi}_s \bar{\varphi}_a \sigma \bar{\sigma} \ldots n_2 \bar{n}_2 \rangle \\ &= -\langle \sigma^* \varphi_s | \sigma \varphi_a \rangle + \langle \sigma^* \varphi_s | \varphi_a \sigma \rangle \\ &\simeq -\tfrac{1}{2}[\langle \sigma^* | \mathscr{J}_{\phi_1} | \sigma \rangle - \langle \sigma^* | \mathscr{J}_{\phi_2} | \sigma \rangle]\end{aligned} \tag{19}$$

if one again neglects the intershell exchange and overlap effects.

One may notice that $\langle \sigma^* | \mathscr{J}_{\phi_2} | \sigma \rangle = -\langle \sigma^* | \mathscr{J}_{\phi_1} | \sigma \rangle$, due to the symmetrical positions of ϕ^2_1 and ϕ^2_2 with respect to the transition dipole $\sigma\sigma^*$, and within the some simplifications, the $\sigma\sigma^*$ excitation leads to an equal interaction. The corresponding second order effect is given by:

$$\varepsilon'^2_{\left(\substack{\sigma \to \sigma^* \\ \varphi_a \to \varphi_s}\right)} = 2 \frac{\langle \sigma^* | \mathscr{J}_{\phi_1} | \sigma \rangle^2}{\Delta E \begin{pmatrix} \sigma^* & \varphi_s \\ \sigma & \varphi_a \end{pmatrix}} \tag{20}$$

$\Delta E \begin{pmatrix} \sigma^* & \varphi_s \\ \sigma & \varphi_a \end{pmatrix} = \Delta E \begin{pmatrix} \sigma^* \\ \sigma \end{pmatrix} + \Delta E \begin{pmatrix} \varphi_s \\ \varphi_a \end{pmatrix}$ in the Moller Plesset definition of the unperturbed hamiltonian, and $-\Delta E \begin{pmatrix} \varphi_s \\ \varphi_a \end{pmatrix} = \langle \varphi_s | \mathscr{F} | \varphi_s \rangle - \langle \varphi_a | \mathscr{F} | \varphi_a \rangle = 2E$, which is negligible with respect to $\Delta E_{\sigma\sigma^*}$. Therefore

$$\varepsilon'^2_{\left(\substack{\sigma \to \sigma^* \\ \varphi_a \to \varphi_s}\right)} \simeq -2 \frac{\langle \sigma^* | \mathscr{J}_{\phi_1} | \sigma \rangle^2}{\Delta E_{\sigma\sigma^*}} = \varepsilon^2_{\sigma\sigma^*} \,. \tag{21}$$

In the excitonic model, the $\sigma\sigma^*$ (resp. $\pi\pi^*$) excitations lead to an important correction on the symmetrical ion energy, representing the instantaneous left-right polarization of the valence shells under the fields created by the localized hole. This effect does not appear directly in the traditional description using symmetry delocalized MO's; *it only appears through a double excitation procedure ($\sigma\sigma^*$ excitation + change of the hole from φ_s to φ_a) which may be called a "correlation effect" between the $\sigma\sigma^*$ transition and the $\varphi_a\varphi_s$ excitation. The use of localized* MO's *leads to a double transfer*

double excitation → single excitation
correlation effect → polarization effect.

As easily verified, the same conclusion holds for the antisymmetric ion $\psi^+_{\varphi_a}$.

4. Excitations towards the Rydberg Levels

4.1. Excitations from the σ and π Levels

There the Rydberg levels are simply virtual MO's orthogonal to the occupied and virtual valence shell MO's. They are not necessarily very diffuse. For instance they may be built from $3s$ and $3p$ AO's with the same exponent as the corresponding $2s$ and $2p$ AO's [15].

The excitations from the σ MO (resp. π MO) towards Rydberg levels which have the same symmetry as the σ^* (resp. π^*) valence MO lead to the same conclusions as the $\sigma \rightarrow \sigma^*$ (resp. $\pi \rightarrow \pi^*$) valence excitations. If R_σ is the antisymmetric σ Rydberg MO, one simply encounters R_{σ^*} instead of σ^* in the expressions (11)–(21); the localized model gives a non-zero effect of single excitations which appears in the delocalized scheme as a double excitation effect.

One may also conceive excitations towards symmetric "Rydberg" levels (for instance a "bonding" R MO built from $3s$ and $3p$ hybrid AO's). The single excitation $\sigma \rightarrow R_\sigma$ having a correct symmetry

$$\begin{aligned} \langle a^+_{R_\sigma} a_\sigma \psi^+_{\varphi_s} | \mathscr{H} | \psi^+_{\varphi_s} \rangle &= \langle R_\sigma | -\mathscr{J}_{\varphi_s} + \mathscr{K}_{\varphi_s} | \sigma \rangle \\ &\simeq \langle R_\sigma | -\mathscr{J}_{\varphi_s} | \sigma \rangle \\ &\simeq \tfrac{1}{2} \langle R_\sigma | -\mathscr{J}_{\phi_1} - \mathscr{J}_{\phi_2} | \sigma \rangle \\ &\simeq \langle R_\sigma | -\mathscr{J}_{\phi_1} | \sigma \rangle \end{aligned} \tag{22}$$

the beta spin excitation giving the same correction (if one neglects the exchange integrals with the core) one gets for the $\sigma \rightarrow R_\sigma$ excitation the 2nd order correction

$$\varepsilon^2_{\sigma \rightarrow R_\sigma} = 2 \langle R_\sigma | \mathscr{J}_{\phi_1} | \sigma \rangle^2 / \Delta E \begin{pmatrix} R_\sigma \\ \sigma \end{pmatrix} \tag{23}$$

in the delocalized scheme. In this scheme the double excitations interaction

$$\langle a^+_{R_\sigma} a_\sigma \psi^+_{\varphi_a} | \mathscr{H} | \psi^+_{\varphi_s} \rangle$$

is zero from symmetry considerations. The localized model introduces the $a^+_{R_\sigma} a_\sigma \psi^+_{\phi_1}$ and $a^+_{R_\sigma} a_\sigma \psi^+_{\phi_2}$ determinants

$$\langle a^+_{R_\sigma} a_\sigma \psi^+_{\phi_1} | \mathscr{H} | \psi^+_{\varphi_s} \rangle \simeq \frac{1}{\sqrt{2}} \langle R_\sigma | -\mathscr{J}_{\phi_1} | \sigma \rangle \, . \tag{24}$$

The beta spin excitation and the $\psi^+_{\phi_2}$ counterpart give the same corrections

$$\varepsilon^2_{\sigma \rightarrow R_\sigma} = 2 \langle R_\sigma | \mathscr{J}_{\phi_1} | \sigma \rangle^2 / \Delta E \begin{pmatrix} R_\sigma \\ \sigma \end{pmatrix} . \tag{25}$$

No significant differences appear between the localized and delocalized scheme, the single excitations giving the correction in both cases.

4.2. Excitation from the Lone Pairs

But we may turn to the localized σ lone pairs n_1 and n_2 and consider for instance the excitation $n_2 \to R_2$ from n_2 to a (3s–3p) hybrid orbital R_2 on the same atom, and same region of space. In the delocalized scheme:

$$\begin{aligned} \langle a^+_{R_2} a_{n_2} \psi^+_{\varphi_s} | \mathscr{H} | \psi^+_{\varphi_s} \rangle &= \langle R_2 | -\mathscr{J}_{\varphi_s} + \mathscr{K}_{\varphi_s} | n_2 \rangle \\ \langle a^+_{\bar{R}_2} a_{\bar{n}_2} \psi^+_{\varphi_s} | \mathscr{H} | \psi^+_{\varphi_s} \rangle &= \langle R_2 | -\mathscr{J}_{\varphi_s} | n_2 \rangle \,. \end{aligned} \tag{26}$$

One may neglect the exchange integrals with the core and develop $\mathscr{J}_{\varphi_s}$

$$\langle R_2 | \mathscr{J}_{\varphi_s} | n_2 \rangle \simeq \tfrac{1}{2} \langle R_2 | \mathscr{J}_{\phi_1} + \mathscr{J}_{\phi_2} | n_2 \rangle \,. \tag{27}$$

The monocentric integral $\langle R_2 | \mathscr{J}_{\phi_2} | n_2 \rangle$ is much larger than the bicentric integral $\langle R_2 | \mathscr{J}_{\phi_2} | n_2 \rangle$ since the last one represents the interaction between the charge $(\phi_1)^2$ on N_1 and the dipole $n_2 R_2$ on N_2. Therefore the two single excitations lead to the second order correction

$$\varepsilon^2_{n_2 \to R_2} = \tfrac{1}{2} \langle R_2 | \mathscr{J}_{\phi_2} | n_2 \rangle^2 / \Delta E \begin{pmatrix} R_2 \\ n_2 \end{pmatrix} . \tag{28}$$

In the delocalized scheme, one may also consider the "double" excitation procedure $a^+_{R_2} a_{n_2} a^+_{\varphi_s} a_{\varphi_a}$

$$\begin{aligned} \langle a^+_{R_2} a_{n_2} \psi^+_{\varphi_a} | \mathscr{H} | \psi^+_{\varphi_s} \rangle &= \langle \varphi_s \bar{\varphi}_s \bar{\varphi}_a \ldots R_2 \bar{n}_2 | \mathscr{H} | \bar{\varphi}_s \varphi_a \bar{\varphi}_a \ldots n_2 \bar{n}_2 \rangle \\ &= -\langle \varphi_s \bar{\varphi}_s \bar{\varphi}_a \ldots R_2 \bar{n}_2 | \mathscr{H} | \varphi_a \bar{\varphi}_s \bar{\varphi}_a \ldots n_2 \bar{n}_2 \rangle \\ &= -\langle \varphi_s R_2 | \varphi_a n_2 \rangle + \langle \varphi_s R_2 | n_2 \varphi_a \rangle \,. \end{aligned} \tag{29}$$

Neglecting again the exchange integral and developing the $\varphi_s \varphi_a$ distribution over the second center, one gets

$$\langle \varphi_s R_2 | \varphi_a n_2 \rangle \simeq \langle R_2 | \mathscr{J}_{\phi_2} | n_2 \rangle / 2$$

and taking into account the β spin analogue one obtains a second order correction:

$$\begin{aligned} \varepsilon^2 \begin{pmatrix} n_2 \to R_2 \\ \varphi_a \to \varphi_s \end{pmatrix} &= \tfrac{1}{2} \langle R_2 | \mathscr{J}_{\phi_2} | n_2 \rangle^2 / \Delta E \begin{pmatrix} R_2 & \varphi_s \\ n_2 & \varphi_a \end{pmatrix} \\ &\simeq \tfrac{1}{2} \langle R_2 | \mathscr{J}_{\phi_2} | n_2 \rangle^2 / \Delta E \begin{pmatrix} R_2 \\ n_2 \end{pmatrix} . \end{aligned} \tag{30}$$

In the delocalized model, the double excitation $\begin{pmatrix} R_2 & \varphi_s \\ n_2 & \varphi_a \end{pmatrix}$ correlation correction is equal to the single excitation $\begin{pmatrix} R_2 \\ n_2 \end{pmatrix}$ polarization correction.

In the localized scheme one must consider the determinants $a^+_{R_2} a_{n_2} \psi^+_{\phi_1}$ and $a^+_{R_2} a_{n_2} \psi_{\phi_2}$. The former gives an interaction

$$\langle a^+_{R_2} a_{n_2} \psi^+_{\phi_1} | \mathscr{H} | \psi^+_{\varphi_s} \rangle \simeq \langle a^+_{\bar{R}_2} a_{\bar{n}_2} \psi^+_{\phi_1} | \mathscr{H} | \psi^+_{\varphi_s} \rangle \simeq \langle R_2 | -\mathscr{J}_{\phi_1} | n_2 \rangle / \sqrt{2} \tag{31}$$

which has been previously neglected with respect to the second interaction, which is monocentric,

$$\begin{aligned} \langle a^+_{R_2} a_{n_2} \psi_{\phi_2} | \mathscr{H} | \psi^+_{\varphi_s} \rangle &\simeq \langle a^+_{\bar{R}_2} a_{\bar{n}_2} \psi^+_{\phi_2} | \mathscr{H} | \psi^+_{\varphi_s} \rangle \\ &\simeq \langle R_2 | -\mathscr{J}_{\phi_2} | n_2 \rangle / \sqrt{2} \,. \end{aligned} \tag{32}$$

In the localized model the lone-pair reorganization by mixture with a correct Rydberg level is given by:

$$\varepsilon^2_{(n_2\to R_2)} = \langle R_2 | \mathscr{J}_{\phi_2} | n_2 \rangle^2 / \Delta E \begin{pmatrix} R_2 \\ n_2 \end{pmatrix} . \tag{33}$$

The lone-pair reorganization correction (or polarization) in the excitonic model is equal to twice the corresponding single excitations correction obtained in the delocalized scheme; the part of the reorganization correction lacking in the delocalized model is simply hidden in a double excitation effect implying both the $n_2 \to R_2$ *process and a change of the core hole from the symmetric to the antisymmetric* MO.

5. Generalization: The Core Ionization in a Chain of *n* Be Atoms

Let us examine the case of a regular chain of n closed shell atoms, in order to see what may be the n-behaviour of the "polarization" energy of the valence shell under the effect of the ionization of the core levels, in both the localized and delocalized schemes. We might consider Ne atoms, but for sake of simplicity, in order to have only one valence shell, we shall consider Be atoms in the $1s^2\, 2s^2$ state. The valence MO's will be localized on the atoms and denoted σ_p. Nearly atomic Rydberg 3s MO's R_p will be introduced to allow the valence shell contraction under the 1s ionization. The 1s MO's may be either localized (ϕ_r) or delocalized (φ_i), leading to two different developments. The ground state determinant may be written in a localized scheme

$$\phi_0 = |\phi_1 \bar{\phi}_1 \ldots \phi_n \bar{\phi}_n \sigma_1 \bar{\sigma}_1 \ldots \sigma_n \bar{\sigma}_n| , \tag{34}$$

or in a core-delocalized, valence-localized scheme

$$\phi_0 = |\varphi_1 \bar{\varphi}_1 \ldots \varphi_n \bar{\varphi}_n \sigma_1 \bar{\sigma}_1 \ldots \sigma_n \bar{\sigma}_n| . \tag{35}$$

(An homogeneously delocalized scheme might be conceived, which is less easy to handle.) The Hückel-type structure of the Fock operator (12) in the basis of localized MO's allows a direct estimation of the delocalized MO's in terms of localized 1s MO's.

$$\varphi_i = \sqrt{\frac{2}{n+1}} \sum_{r=1}^{n} \sin \frac{i\pi r}{n+1} \phi_r \tag{36}$$

and of the delocalized description of the ions

$$\psi^+_{\varphi_i} = \sqrt{\frac{2}{n+1}} \sum_{r=1}^{n} \sin \frac{i\pi r}{n+1} \psi^+_{\phi_r} \tag{37}$$

with

$$\psi^+_{\varphi_i} = a_{\varphi_i} \phi_0 , \qquad \psi^+_{\phi_r} = a_{\phi_r} \phi_0$$

and

$$\langle \psi^+_{\varphi_i} | \mathscr{H} | \psi^+_{\varphi_j} \rangle = 0 .$$

In the localized scheme, the basis determinants of the CI involving the valence shell reorganization are the determinants $a^+_{R_p} a_{\sigma_p} \psi^+_{\phi_r}$ with an ionization of the 1s core of the atom r and a valence excitation on the atom p. The interaction between such a determinant and an ionic zeroth order wave function is:

$$\langle a^+_{R_p} a_{\sigma_p} \psi^+_{\phi_r} | \mathscr{H} | \psi^+_{\varphi_i} \rangle = \sum_{s=1}^{n} \sqrt{\frac{2}{n+1}} \sin \frac{i\pi s}{n+1} \langle a^+_{R_p} a_{\sigma_p} \psi^+_{\phi_r} | \mathscr{H} | \psi^+_{\phi_s} \rangle , \tag{38}$$

$$\langle a^+_{R_p} a_{\sigma_p} \psi^+_{\phi_r} | \mathscr{H} | \psi^+_{\phi_s} \rangle = - \langle R_p \phi_s | \sigma_p \phi_r \rangle \tag{39}$$

which implies the negligible overlap distribution $\phi_r \phi_s$, except for $r = s$. In this case

$$\langle R_p \phi_r | \sigma_p \phi_r \rangle = \langle R_p | \mathscr{J}_r | \sigma_p \rangle = \alpha_{rp} \tag{40}$$

represents the interaction between the $2s \rightarrow 3s$ transition quadrupole on the atom p with the hole charge on the atom r. These integrals decreasing as R_{rp}^{-3} one may keep only the local interactions $r = p$ $(\alpha_{rp} = \alpha)$. Therefore

$$\langle a^+_{R_p} a_{\sigma_p} \psi^+_{\phi_p} | \mathscr{H} | \psi^+_{\varphi_i} \rangle = - \sqrt{\frac{2}{n+1}} \sin \left(\frac{i\pi p}{n+1} \right) \times \alpha . \tag{41}$$

The second order effect of the valence shell excitations will be given by a summation over the atoms

$$\varepsilon^2 = \sum_{p=1}^{n} \frac{2}{n+1} \sin^2 \left(\frac{i\pi p}{n+1} \right) \frac{\alpha^2}{\Delta E \begin{pmatrix} R_r \\ \sigma_r \end{pmatrix}} . \tag{42}$$

As well known

$$\sum_{p=1}^{n} \sin^2 x = \frac{n}{2} - \frac{\cos(n+1)x \sin nx}{2 \sin x} , \tag{43}$$

and

$$\sum_{p=1}^{n} \sin^2 \frac{i\pi p}{n+1} = \frac{n+1}{2} . \tag{44}$$

Therefore

$$\varepsilon^2 = \frac{\alpha^2}{\Delta E \begin{pmatrix} R \\ \sigma \end{pmatrix}} \tag{45}$$

if $\Delta E \begin{pmatrix} R_r \\ \sigma_r \end{pmatrix} = \Delta E \begin{pmatrix} R \\ \sigma \end{pmatrix} \forall r$ (transferability of the local transition energies).

The second order polarization effect of the valence shells under the 1*s ionization is independant on the number of atoms.*

We may turn back to the delocalized scheme. Here the valence polarization might appear as the result of the single excitation processes $\sigma_p \rightarrow R_p$ on the zeroth order determinant $\psi^+_{\varphi_i}$

$$\langle a^+_{R_p} a_{\sigma_p} \psi^+_{\varphi_i} | \mathscr{H} | \psi^+_{\varphi_i} \rangle = \langle R_p | - \mathscr{J}_{\varphi_i} | \sigma_p \rangle \tag{46}$$

with

$$\mathscr{J}_{\varphi_i} = \sum_{s=1}^{n} \frac{2}{n+1} \sin^2 \left(\frac{i\pi s}{n+1} \right) \mathscr{J}_{\phi_s}$$

if one neglects the overlap distributions. Making the same approximation as before

$$(\langle R_p | - \mathscr{J}_{\phi_s} | \sigma_p \rangle = \alpha \delta_{sp}) ,$$

$$\langle a^+_{R_p} a_{\sigma_p} \psi^+_{\varphi_i} | \mathscr{H} | \psi^+_{\varphi_i} \rangle = \frac{2\alpha}{n+1} \sin^2 \frac{i\pi p}{n+1} \tag{47}$$

The valence single excitations lead to a total second order correction

$$\varepsilon^2 = \sum_{p=1}^{n} \frac{\langle a^+_{R_p} a_{\sigma_p} \psi^+_{\varphi_i} | \mathscr{H} | \psi^+_{\varphi_i} \rangle^2}{\Delta E \begin{pmatrix} R_p \\ \sigma_p \end{pmatrix}} = \frac{\sigma^2}{\Delta E \begin{pmatrix} R \\ \sigma \end{pmatrix}} \frac{4}{(n+1)^2} \sum_{p=1}^{n} \sin^4 \frac{i\pi p}{n+1} . \tag{48}$$

A direct calculation leads to

$$\sum_{p=1}^{n} \sin^4 \frac{i\pi p}{n+1} = \frac{3}{8}(n+1) \tag{49}$$

and therefore

$$E^2 = \frac{\alpha^2}{\Delta E \begin{pmatrix} R \\ \sigma \end{pmatrix}} \frac{3}{2(n+1)} . \tag{50}$$

The valence shell $\begin{pmatrix} R \\ \sigma \end{pmatrix}$ *single excitations on the delocalized description of the ion lead to a vanishing polarization effect decreasing as* 3/2*n when the number n of atoms increases.*

Again the constant polarization effect obtained in the localized picture may be obtained in the delocalized picture through "double excitation" processes involving hole changes, namely through the determinants,

$$a^+_{R_p} a_{\sigma_p} \psi^+_{\varphi_j} = a^+_{R_p} a_{\sigma_p} a^+_{\varphi_i} a_{\varphi_j} \psi^+_{\varphi_i} . \tag{51}$$

Indeed

$$\begin{aligned} \langle a^+_{R_p} a_{\sigma_p} \psi^+_{\varphi_j} | \mathscr{H} | \psi^+_{\varphi_i} \rangle \quad & - \langle R_p \varphi_i | \sigma_p \varphi_j \rangle \\ & = - \sum_{r=1}^{n} \frac{2}{n+1} \sin \frac{i\pi r}{n+1} \sin \frac{j\pi r}{n+1} \langle R_p | - \mathscr{J}_{\phi_r} | \sigma_p \rangle \\ & \simeq - \sin \frac{i\pi p}{n+1} \sin \frac{j\pi p}{n+1} \frac{2\alpha}{n+1} . \end{aligned} \tag{52}$$

Therefore the summation over all these determinants is a double summation, over *p* and *j*, and leads to a second order correction

$$\varepsilon^2 = \sum_{r=1}^{n} \sum_{j=1}^{n} \frac{\langle a^+_{R_p} a_{\sigma_p} \psi^+_{\varphi_j} | \mathscr{H} | \psi^+_{\varphi_i} \rangle^2}{\Delta E \begin{pmatrix} R_p & \varphi_j \\ \sigma_p & \varphi_i \end{pmatrix}} . \tag{53}$$

Due to the near degeneracy between the core levels,

$$\Delta E \begin{pmatrix} R_p & \varphi_j \\ \sigma_p & \varphi_i \end{pmatrix} \simeq \Delta E \begin{pmatrix} R_p \\ \sigma_p \end{pmatrix} = \Delta E \begin{pmatrix} R \\ \sigma \end{pmatrix} , \tag{54}$$

and the second order effect is given by

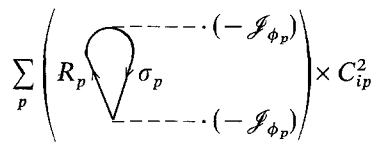
$$\varepsilon^2 = \frac{4\alpha^2}{(n+1)^2 \Delta E \begin{pmatrix} R \\ \sigma \end{pmatrix}} \sum_p \sum_j \sin^2 \frac{i\pi p}{n+1} \sin^2 \frac{j\pi p}{n+1} . \tag{55}$$

Since $\sum_{j=1}^{n} \sin^2 \frac{j\pi p}{n+1} = \frac{n+1}{2}$ (cf. supra), the two summations split and reduce to $\left(\frac{n+1}{2}\right)^2$. Therefore

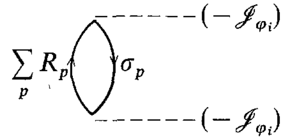
$$\varepsilon^2 = \frac{\alpha^2}{\Delta E\binom{R}{\sigma}}. \tag{56}$$

The total second order effect of the valence excitations is independant on the number of atoms and equal to the localized contribution if one allows a simultaneous core level interchange (displacement of the core "quasi-hole").

Therefore the valence-shell reorganization which appeared clearly in the localized picture is a sum of equiprobable local effects,

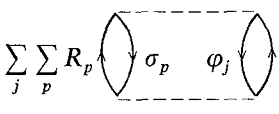


is the result of single and double excitation effects in the delocalized model. The single excitations



are the only effect for the isolated atom but their contribution decreases as $\frac{1}{n}$ when n increases,

while the double excitations



give the dominant effect for large n. The sum of these two types of corrections is independant of the number of atoms and the considered $1s$ level.

6. Discussion and Concluding Remarks

The present work illustrates in detail on a peculiar example the general and overall equivalence of localized and delocalized pictures. The difference between them is a matter of convenience and interpretation. The polarization of the valence shells under a core ionization are mainly due to local repolarizations (single excitations) under local ionization in the localized picture while these single excitations only give a decreasing part of the second order effect in the delocalized picture; in this picture the effect implies "double excitations"[2], with a change in the "ejected quasiparticle". The superiority of the localized scheme, if any, is merely its greater simplicity for an interpretation.

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[2] One may notice that the displacement of the effect from a single excitation effect to a double excitation effect is not in contradiction with the stability of the restriction of the hamiltonian to the space of the single excitations. This stability refers to the ground state picture; from this point of view the determinants $\psi^+_{\phi_p}$ or $\psi^+_{\varphi_i}$ are singly excited; the determinants $a^+_{R_p} a_{\sigma_p} \psi^+_{\phi_p}$ or $a^+_{R_p} a_{\sigma_p} \psi^+_{\varphi_i}$ are doubly excited, and the determinants $a^+_{R_p} a_{\sigma_p} a^+_{\varphi_j} a^+_{\varphi_i} \psi^+_{\varphi_i} = a^+_{R_p} a_{\sigma_p} \psi^+_{\varphi_j}$ also are doubly excited with respect to ϕ^0_0. The single or double excitations in our text refer to the zeroth order description of the ion $\psi^+_{\varphi_i}$.

As mentioned briefly in the introduction of this paper, an interesting discussion occured about the localized or delocalized nature of the core-hole. Snyder [4] actually pointed out that the repolarization effect on a localized non-symmetrical (and therefore non-stationary) wave-function $\psi^+_{\phi_r}$ was larger than the corresponding effect on the delocalized ionic wave-function $\psi^+_{\varphi_i}$. He added some time considerations which will be discussed below. Bagus and Schaeffer [5] performed Hartree-Fock calculation on O_2^+, and obtained lower energies for unsymmetrical wave-functions in which the hole is localized. They concluded from this Hartree-Fock instability that the "hole state is localized on one of the two oxygen atoms". The present analysis allows a few comments about these statements.

(1) Quantum mechanics does not know single particle states or hole-states in a many-body system. The states refer to the n-particles and the practical successes and nearly monopolistic situation of the Hartree-Fock approximation do not give any physical reality to the molecular orbitals.

(2) The present work allows a clear interpretation of the Hartree-Fock instability verified for the O_2^+ ion. The second order single particle excitations are included in a HF scheme while the double excitations second order corrections are not. Therefore the HF calculation in the basis of symmetry delocalized MO only includes a small part of the total repolarization effect. An unrestricted Hartree-Fock calculation without the symmetry constraints lacks the benefit of the hole delocalization given by symmetry MO's, but includes the local single excitations effect i.e. the total repolarization effect of the valence shell. In the case of very strongly localized AO's, such as the 1s orbitals, the delocalization of the hole is much smaller than the repolarization effect and the local stable determinant is lower in energy. But the solution of the Schrödinger equation is independant on the basis of MO's used to build the N-particle wave-functions. If one is interested in this solution one must remember that it must be an eigen-state of the symmetry operators which commutes with the hamiltonian. A proper solution is symmetrical or antisymmetrical with respect to the center of symmetry of the molecule. If the HF process gives a stable unsymmetrical solution (hole on the right side), it necessarily gives the degenerate symmetric solution (hole on the left side), and a better solution, symmetrical or antisymmetrical is obtained by a linear combination of the left-localized and right-localized unrestricted Hartree-Fock determinants. This interaction removes the degeneracy and reintroduces the core delocalization effect. However the process (or the projection on the symmetrical subspaces) is quite involved.

(3) The MO's are only intermediates in the calculation of the exact wave-function which may be expressed as well in terms of localized or delocalized MO's. The present paper shows that the same valence shell effect is obtained in both models, the only changes concerning its more are less hidden place in the CI calculation and its qualitative verbal interpretation in terms of repolarization or correlation effect. The localized description, although uncommon, has the practical advantage of a clear exhibition of the phenomenon as a sum of local effects while the delocalized picture brings it through complex [valence excitation + hole change] processes.

(4) The consideration of the Hartree-Fock unstability to answer the physical question of the localization of the hole is meaningless. The wave-function of a stationary state concerns a statistical set of molecules (16) and *must* therefore give equal probabilities for the equivalent sites of the molecule. The N_2^+ problem does not differ from that point of view from the H_2^+ problem. At *all distances* in H_2^+ the electron has equal probabilities to be on the left or the right half spaces but if one studies the variance of the operator number of particles in the left half space, one finds equal probabilities to have zero electron or one electron; on each molecule the electron is either in the right or in the left half spaces, and the same statement is valid for the position of the core hole of the N_2^+ ion.

The question of the physical localization of the core hole, as well as the question of the position of the electron in H_2^+, may only be a time problem. The question may be analyzed in two different directions. One may wonder about the time evolution in a stationary state, using the operators which gives the probability to find a particle in the volume B at time t_1 if there was a particle in the volume A at time t_0, as recently proposed by Claverie and Diner [17]. One may also assume that the initial hole is localized (and therefore does not correspond to an eigenstate of H) and analyse the time evolution which insures the delocalization of the hole (using a time dependant perturbation theory). Although he refered to the pseudo-uncertainty relation $\Delta E \cdot \Delta t \geqq h$, Snyder's most interesting argument [4] concerned this problem of time, stating that the hole delocalization from a well localized state required more time than the life-time of this highly excited state. This relevant question, which requires a non-stationary wave-function, cannot be answered of course, by the analysis of the polarization effect in a localized picture or the discovery of an unstability in the Hartree-Fock calculation.

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