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# Localized Orbitals for the Oxygen and Nitric Oxide Molecules

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Localized orbitals are derived for the ground states of the oxygen and nitric oxide molecules by applying localization methods separately to the orbitals containing electrons of alpha- and beta-spin. Both the intrinsic energy localization and the uniform localization methods are used. The resulting localized orbitals are in good agreement with the formulae suggested by Linnett.

Für die Grundzustände der Moleküle $O_2$ und NO werden lokalisierte Orbitale abgeleitet, indem die Lokalisierungsmethoden getrennt für die Orbitale mit $\alpha$- und $\beta$-Spin angewendet werden. Dabei werden sowohl die eigentlichen Energielokalisierungsmethoden als auch die gleichförmigen Lokalisierungsmethoden benutzt. Die erhaltenen lokalisierten Orbitale stimmen gut mit den von Linnett vorgeschlagenen Formeln überein.

Obtention d'orbitales localisées pour l'état fondamental des molécules d'oxygène et d'oxyde nitreux par localisation indépendante des orbitales de spin $\alpha$ et des orbitales de spin $\beta$. Emploi simultané de la localisation selon l'énergie intrinsèque et de la localisation uniforme. Les orbitales localisées résultantes sont en bon accord avec les formules suggérées par Linnett.

## 1. Introduction

There is currently considerable interest in the transformation of SCF molecular orbitals to localized orbitals which correspond to bonding, lone pair and inner shell orbitals used in the qualitative discussion of chemical bonding [1–4]. So far consideration has been restricted to wavefunctions involving only doubly filled orbitals. Although Peters [3] considered some odd electron systems, localization was restricted to the doubly-filled sigma-orbitals. There have been no applications to odd electron molecules such as oxygen and nitric oxide. Presumably this is because we are not able to write down single electron pair bond structures for these systems. However, Linnett [5] has suggested that the alpha- and beta-electrons should be considered separately in these molecules and has shown how single formulae can be written to represent their electronic structures. Therefore it should be possible to derive localized molecular orbitals for these systems by localizing separately the orbitals containing alpha- and beta-electrons. This paper describes the application of this idea to the oxygen and nitric oxide molecules.

## 2. Method of Localization

Ruedenberg [6] has classified localization criteria as "intrinsic" and "external". Intrinsic criteria depend only on the molecular orbitals themselves, whereas external criteria require the localized orbitals to satisfy some additional criteria. Murrell *et al.* [2] have compared various procedures and concluded that of the intrinsic criteria, the minimisation of the sum $\left(\sum_{i<j} J_{ij}\right)$ of the coulomb integrals $J_{ij}$ between orbitals $i$ and $j$ is generally the most satisfactory. This method was originally suggested by Lennard-Jones and Pople [7] and has been used extensively by Edmiston and Ruedenberg [1]. However this method is

Table 1. *Localized orbitals for the oxygen molecule*

| | $1S_a$ | $2S_a$ | $2p\sigma_a$ | $2p\pi_a$ | $2p\bar{\pi}_a$ | $1S_b$ | $2S_b$ | $2p\sigma_b$ | $2p\pi_b$ | $2p\bar{\pi}_b$ |
|---|---|---|---|---|---|---|---|---|---|---|
| A. *Energy localization* | | | | | | | | | | |
| (i) *Alpha-spins* | | | | | | | | | | |
| *i*A | 1.022 | −0.132 | 0.027 | −0.000 | −0.000 | −0.000 | 0.011 | −0.009 | 0.000 | 0.000 |
| *i*B | 0.000 | −0.011 | 0.009 | 0.000 | 0.000 | −1.022 | 0.132 | −0.027 | −0.000 | 0.000 |
| *nb*A | −0.056 | 0.576 | −0.184 | −0.366 | 0.737 | 0.005 | −0.060 | −0.070 | 0.027 | −0.053 |
| *nb*A | −0.057 | 0.577 | −0.184 | 0.821 | −0.052 | 0.005 | −0.060 | −0.070 | −0.060 | 0.004 |
| *nb*A | −0.056 | 0.576 | −0.184 | −0.456 | −0.684 | 0.005 | −0.060 | −0.070 | 0.034 | 0.050 |
| *nb*B | 0.005 | −0.060 | −0.070 | −0.035 | 0.048 | −0.056 | 0.576 | −0.184 | 0.482 | −0.666 |
| *nb*B | −0.005 | 0.060 | 0.070 | 0.025 | 0.054 | 0.056 | −0.576 | 0.184 | −0.337 | −0.750 |
| *nb*B | −0.005 | 0.060 | 0.070 | −0.060 | −0.006 | 0.057 | −0.577 | 0.184 | 0.819 | 0.084 |
| *b* | 0.034 | −0.173 | −0.556 | −0.000 | 0.000 | 0.034 | −0.173 | −0.556 | −0.000 | 0.000 |
| (ii) *Beta-spins* | | | | | | | | | | |
| *i*A | −1.022 | 0.126 | −0.026 | 0.000 | 0.000 | 0.000 | −0.010 | 0.009 | 0.000 | 0.000 |
| *i*B | 0.000 | −0.010 | 0.009 | 0.000 | 0.000 | −1.022 | 0.126 | −0.026 | 0.000 | 0.000 |
| *nb*A | 0.093 | −0.933 | 0.437 | 0.000 | −0.000 | −0.020 | 0.170 | 0.239 | 0.000 | −0.000 |
| *nb*B | 0.020 | −0.170 | −0.239 | −0.000 | 0.000 | −0.093 | 0.933 | −0.437 | −0.000 | 0.000 |
| *b* | −0.032 | 0.216 | 0.244 | −0.293 | 0.452 | −0.032 | 0.216 | 0.244 | −0.293 | 0.452 |
| *b* | 0.032 | −0.216 | 0.242 | −0.539 | 0.028 | 0.032 | −0.216 | −0.242 | −0.539 | 0.028 |
| *b* | 0.032 | −0.216 | −0.243 | 0.244 | 0.480 | 0.032 | −0.216 | −0.243 | 0.244 | 0.480 |
| B. *Uniform localization* | | | | | | | | | | |
| (i) *Alpha-spins* | | | | | | | | | | |
| *i*A | 1.020 | −0.113 | 0.021 | 0.000 | 0.000 | 0.000 | 0.007 | −0.011 | 0.000 | 0.000 |
| *i*B | 0.000 | 0.007 | −0.011 | 0.000 | 0.000 | 1.020 | −0.113 | 0.021 | 0.000 | 0.000 |
| *nb*A | −0.068 | 0.575 | −0.191 | 0.582 | 0.582 | 0.006 | −0.062 | −0.076 | −0.043 | −0.043 |
| *nb*A | −0.068 | 0.575 | −0.191 | 0.213 | −0.795 | 0.006 | −0.062 | −0.076 | −0.016 | 0.059 |
| *nb*A | −0.068 | 0.575 | −0.191 | −0.795 | 0.213 | 0.006 | −0.062 | −0.076 | 0.059 | −0.016 |
| *nb*B | 0.006 | −0.062 | −0.076 | −0.043 | −0.043 | −0.068 | 0.575 | −0.191 | 0.582 | 0.582 |
| *nb*B | 0.006 | −0.062 | −0.076 | −0.016 | 0.059 | −0.068 | 0.575 | −0.191 | 0.213 | −0.795 |
| *nb*B | 0.006 | −0.062 | −0.076 | 0.059 | −0.016 | −0.068 | 0.575 | −0.191 | −0.795 | 0.213 |
| *b* | −0.036 | 0.193 | 0.546 | 0.000 | 0.000 | −0.036 | 0.193 | 0.546 | 0.000 | 0.000 |
| (ii) *Beta-spins* | | | | | | | | | | |
| *i*A | 1.020 | −0.113 | 0.021 | 0.000 | 0.000 | 0.000 | 0.007 | −0.011 | −0.000 | 0.000 |
| *i*B | 0.000 | 0.007 | −0.011 | 0.000 | 0.000 | 1.020 | −0.113 | 0.021 | 0.000 | 0.000 |
| *nb*A | −0.117 | 0.997 | −0.331 | 0.000 | 0.000 | 0.011 | −0.108 | −0.132 | 0.000 | 0.000 |
| *nb*B | 0.011 | −0.108 | −0.132 | 0.000 | 0.000 | −0.117 | 0.997 | −0.331 | −0.000 | 0.000 |
| *b* | −0.021 | 0.111 | 0.315 | 0.539 | 0.000 | −0.021 | 0.111 | 0.315 | 0.539 | 0.000 |
| *b* | −0.021 | 0.111 | 0.315 | −0.270 | −0.467 | −0.021 | 0.111 | 0.315 | −0.270 | −0.467 |
| *b* | −0.021 | 0.111 | 0.315 | −0.270 | 0.467 | −0.021 | 0.111 | 0.315 | −0.270 | 0.467 |

*iA*, *nb*A refer to inner shell and non bonding orbitals on atom A.
*b* refers to a bonding orbital.

rather tedious. Recently Magnasco and Perico [4] have suggested an external criterion in which they uniformly localize the molecular orbitals by maximising the sum of local orbital populations for localized bonding orbitals, lone pair orbitals and inner shells. This method gives results in good agreement with those of Edmiston and Ruedenberg with much less computing time. Both methods are used in this paper.

## 3. The Oxygen Molecule

The wavefunction for the ${}^3\Sigma_g^-$ ground state of the oxygen molecule can be written as a single Slater determinant in terms of real orbitals

$$\Psi = |1\sigma_g^2 2\sigma_g^2 3\sigma_g^2 1\sigma_u^2 2\sigma_u^2 1\pi_u^2 1\bar{\pi}_u^2 1\pi_g 1\bar{\pi}_g| .$$

The localized orbitals for the electrons of alpha- and beta-spin can therefore be derived straightforwardly.

Minimal basis set SCF – LCAO molecular orbitals were taken from the work of Sahni and Lorenzo [8]. The orthogonalized 2*s* orbital was replaced by the appropriate combination of Slater 1*s* and 2*s* orbitals. Sahni and Lorenzo also report wavefunctions for a spin polarized calculation in which different orbitals are taken for the electrons of alpha- and beta-spin. We also consider the localization of these orbitals in order to see if we can understand qualitatively how the spin polarized treatment allows for electron correlation. The coulomb, hybrid and exchange integrals over atomic orbitals required for the intrinsic energy localization were calculated with the Midiat program [9]. The overlap integrals required for the uniform localization were calculated using subroutines from a program by Segal [10].

Table 2. *Energy localized spin-polarized orbitals for the oxygen molecule*

| | $1S_a$ | $2S_a$ | $2p\sigma_a$ | $2p\pi_a$ | $2p\bar{\pi}_a$ | $1S_b$ | $2S_b$ | $2p\sigma_b$ | $2p\pi_b$ | $2p\bar{\pi}_b$ |
|---|---|---|---|---|---|---|---|---|---|---|
| (i) *Alpha-spins* | | | | | | | | | | |
| *i*A | −1.022 | 0.133 | −0.027 | 0.000 | 0.000 | 0.000 | −0.012 | 0.008 | 0.000 | 0.000 |
| *i*B | 0.000 | −0.011 | 0.008 | 0.000 | 0.000 | −1.022 | 0.133 | −0.027 | 0.000 | 0.000 |
| *nb*A | 0.057 | −0.578 | 0.181 | 0.372 | −0.735 | −0.005 | 0.061 | 0.071 | −0.027 | 0.054 |
| *nb*A | 0.057 | −0.578 | 0.181 | −0.822 | 0.045 | −0.005 | 0.061 | 0.071 | 0.061 | −0.003 |
| *nb*A | −0.057 | 0.578 | −0.181 | −0.450 | −0.689 | 0.005 | −0.061 | −0.071 | 0.033 | 0.051 |
| *nb*B | 0.005 | −0.061 | −0.071 | −0.035 | 0.049 | 0.057 | 0.578 | −0.181 | 0.480 | −0.669 |
| *nb*B | 0.005 | −0.061 | −0.071 | 0.060 | 0.006 | −0.057 | 0.578 | −0.181 | −0.819 | −0.081 |
| *nb*B | −0.005 | 0.061 | 0.071 | 0.025 | 0.055 | 0.057 | −0.578 | 0.181 | −0.339 | −0.750 |
| *b* | 0.034 | −0.171 | −0.557 | 0.000 | 0.000 | 0.034 | −0.171 | −0.557 | −0.000 | 0.000 |
| (ii) *Beta-spins* | | | | | | | | | | |
| *i*A | 1.021 | −0.122 | 0.030 | 0.000 | 0.000 | 0.000 | 0.005 | −0.012 | 0.000 | 0.000 |
| *i*B | 0.000 | 0.005 | −0.012 | 0.000 | 0.000 | 1.021 | −0.122 | 0.030 | 0.000 | 0.000 |
| *nb*A | 0.091 | −0.909 | 0.475 | 0.000 | −0.000 | −0.019 | 0.152 | 0.207 | 0.000 | −0.000 |
| *nb*B | 0.019 | −0.152 | −0.207 | −0.000 | 0.000 | −0.091 | 0.909 | −0.475 | −0.000 | 0.000 |
| *b* | −0.033 | 0.220 | 0.241 | −0.293 | 0.452 | −0.033 | 0.220 | 0.241 | −0.293 | 0.452 |
| *b* | 0.032 | −0.219 | −0.239 | −0.539 | −0.028 | 0.032 | −0.219 | −0.239 | −0.539 | −0.028 |
| *b* | 0.032 | −0.220 | −0.240 | 0.245 | 0.480 | 0.032 | −0.220 | −0.240 | 0.245 | 0.480 |

Table 3. *Transformation matrices — oxygen molecule*

| | $1\sigma_g$ | $2\sigma_g$ | $3\sigma_g$ | $1\sigma_u$ | $2\sigma_u$ | $1\pi_u$ | $1\bar{\pi}_u$ | $1\pi_g$ | $1\bar{\pi}_g$ |
|---|---|---|---|---|---|---|---|---|---|
| A. *Energy localization* | | | | | | | | | |
| (i) *Alpha-spins* | | | | | | | | | |
| *i*A | 0.700 | −0.095 | −0.038 | 0.699 | −0.105 | 0.000 | −0.000 | −0.000 | −0.000 |
| *i*B | −0.700 | 0.095 | 0.038 | 0.699 | −0.105 | −0.000 | 0.000 | 0.000 | 0.000 |
| *nb*A | 0.055 | 0.294 | 0.277 | 0.060 | 0.404 | −0.256 | 0.517 | −0.256 | 0.517 |
| *nb*A | 0.055 | 0.295 | 0.277 | 0.060 | 0.404 | 0.576 | −0.037 | 0.576 | −0.037 |
| *nb*A | 0.055 | 0.294 | 0.277 | 0.060 | 0.404 | 0.320 | −0.481 | −0.320 | −0.481 |
| *nb*B | 0.055 | 0.294 | 0.277 | −0.060 | −0.404 | 0.338 | −0.468 | −0.338 | −0.468 |
| *nb*B | −0.055 | −0.295 | −0.277 | 0.060 | 0.404 | 0.574 | 0.059 | −0.574 | −0.059 |
| *nb*B | −0.055 | −0.294 | −0.277 | 0.060 | 0.404 | −0.236 | −0.527 | 0.236 | 0.527 |
| *b* | −0.052 | −0.680 | 0.732 | 0.000 | 0.000 | −0.000 | 0.000 | 0.000 | 0.000 |
| (ii) *Beta-spins* | | | | | | | | | |
| *i*A | −0.700 | 0.092 | 0.036 | −0.700 | 0.100 | 0.000 | 0.000 | | |
| *i*B | −0.700 | 0.092 | 0.036 | 0.700 | 0.100 | 0.000 | −0.000 | | |
| *nb*A | −0.074 | −0.322 | −0.625 | −0.100 | −0.700 | 0.000 | −0.000 | | |
| *nb*B | 0.074 | 0.322 | 0.625 | −0.100 | −0.700 | −0.000 | 0.000 | | |
| *b* | 0.053 | 0.510 | −0.269 | 0.000 | −0.000 | −0.443 | 0.685 | | |
| *b* | −0.053 | −0.508 | 0.267 | 0.000 | 0.000 | −0.816 | −0.042 | | |
| *b* | −0.053 | −0.509 | 0.268 | 0.000 | −0.000 | 0.370 | 0.728 | | |
| B. *Uniform localization* | | | | | | | | | |
| (i) *Alpha-spins* | | | | | | | | | |
| *i*A | 0.701 | −0.086 | −0.029 | 0.701 | −0.090 | 0.000 | 0.000 | 0.000 | 0.000 |
| *i*B | 0.701 | −0.086 | −0.029 | −0.701 | 0.090 | 0.000 | 0.000 | 0.000 | 0.000 |
| *nb*A | 0.047 | 0.287 | 0.287 | 0.052 | 0.405 | 0.408 | 0.408 | 0.408 | 0.408 |
| *nb*A | 0.047 | 0.287 | 0.287 | 0.052 | 0.405 | 0.149 | −0.558 | 0.149 | −0.558 |
| *nb*A | 0.047 | 0.287 | 0.287 | 0.052 | 0.405 | −0.558 | 0.149 | −0.558 | 0.149 |
| *nb*B | 0.047 | 0.287 | 0.287 | −0.052 | −0.405 | −0.408 | −0.408 | 0.408 | 0.408 |
| *nb*B | 0.047 | 0.287 | 0.287 | −0.052 | −0.405 | −0.149 | 0.558 | 0.149 | −0.558 |
| *nb*B | 0.047 | 0.287 | 0.287 | −0.052 | −0.405 | 0.558 | −0.149 | −0.558 | 0.149 |
| *b* | 0.057 | 0.701 | −0.711 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| (ii) *Beta-spins* | | | | | | | | | |
| *i*A | 0.701 | −0.086 | −0.029 | 0.710 | −0.090 | 0.000 | 0.000 | | |
| *i*B | 0.701 | −0.086 | −0.029 | −0.710 | 0.090 | 0.000 | 0.000 | | |
| *nb*A | 0.082 | 0.497 | 0.497 | 0.090 | 0.701 | 0.000 | 0.000 | | |
| *nb*B | 0.082 | 0.497 | 0.497 | −0.090 | −0.701 | 0.000 | 0.000 | | |
| *b* | 0.033 | 0.405 | −0.410 | 0.000 | −0.000 | 0.816 | 0.000 | | |
| *b* | 0.033 | 0.405 | −0.410 | 0.000 | −0.000 | −0.408 | −0.707 | | |
| *b* | 0.033 | 0.405 | −0.410 | 0.000 | −0.000 | −0.408 | 0.707 | | |

Table 1 contains the localized orbitals obtained by both methods for the non-spin polarized case. Energy localized orbitals for the spin polarized wavefunctions are in Table 2. The transformation matrices for the non-spin polarized orbitals are in Table 3. Because there is no significant difference between the localized orbitals for the spin polarized and non-spin polarized cases, the spin polarized transformation matrices are not reported.

A comparison of the coefficients for the $\sigma$-orbitals shows that both methods give similar results although there is a considerable difference in the $s/p\sigma$ ratio

Table 4. *Energy localized orbitals after rotation about molecular axis*

| | | $1S_a$ | $2S_a$ | $2p\sigma_a$ | $2p\pi_a$ | $2p\bar{\pi}_a$ | $1S_b$ | $2S_b$ | $2p\sigma_b$ | $2p\pi_b$ | $2p\bar{\pi}_b$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Alpha-orbitals* | | | | | | | | | | | |
| *nb*A | 1 | −0.056 | 0.576 | −0.184 | 0.212 | 0.795 | 0.005 | −0.060 | −0.070 | −0.015 | −0.058 |
| | 2 | −0.057 | 0.577 | −0.184 | 0.582 | −0.582 | 0.005 | −0.060 | −0.070 | −0.043 | 0.043 |
| | 3 | −0.056 | 0.576 | −0.184 | −0.795 | −0.212 | 0.005 | −0.060 | −0.070 | 0.058 | 0.015 |
| *nb*B | 1 | 0.005 | −0.060 | −0.070 | 0.015 | 0.058 | −0.056 | 0.576 | −0.184 | −0.212 | −0.795 |
| | 2 | −0.005 | 0.060 | 0.070 | −0.043 | 0.043 | 0.057 | −0.577 | 0.184 | 0.582 | −0.582 |
| | 3 | −0.005 | 0.060 | 0.070 | 0.058 | 0.015 | 0.056 | −0.576 | 0.184 | −0.795 | −0.212 |
| *Beta-orbitals* | | | | | | | | | | | |
| *b* | 1 | −0.032 | 0.216 | 0.244 | −0.269 | 0.467 | −0.032 | 0.216 | 0.244 | −0.269 | 0.467 |
| | 2 | 0.032 | −0.216 | −0.242 | −0.540 | 0.000 | 0.032 | −0.216 | −0.242 | −0.540 | 0.000 |
| | 3 | 0.032 | −0.216 | −0.243 | 0.269 | 0.467 | 0.032 | −0.216 | −0.243 | 0.269 | 0.467 |

for the beta-orbitals. Magnasco and Perico [4] noted that deviations in the $s/p\sigma$ ratio varied from molecule to molecule. In order to make a direct comparison of the coefficients of the $\pi$-orbitals it is necessary to rotate one set about the molecular axis. It may be noted that in the energy localization the equivalent trigonal orbitals undergo a small rotation such that the orbital which is principally $2p\pi$ contains a small amount of $2p\bar{\pi}$. A similar rotation can be observed in the results of Edmiston and Ruedenberg for $N_2$ and $F_2$ [1]. Table 4 contains the result of performing rotations on the energy localized orbitals for the non-spin polarized case. The coefficients for the $\pi$-orbitals are seen to be in excellent agreement with those obtained by uniform localization.

The localized orbitals are in good agreement with Linnett's formula for the oxygen molecule [5]. For the electrons of alpha-spin there are two inner shell orbitals consisting mainly of a 1*s* orbital and three non-bonding orbitals on each atom and one bonding orbital. The four valence shell orbitals on each atom are approximately tetrahedrally disposed. Localization of the orbitals containing the electrons of beta-spin yields two inner shell orbitals, three "banana" bonding orbitals and one non-bonding orbital on each atom. Again the angles between the four valence orbitals on each atom are essentially tetrahedral.

One might expect the energy localized non-bonding orbitals for the alpha-electrons to adopt a staggered conformation. However, the resulting orbitals are almost eclipsed. Edmiston and Ruedenberg observed that the sum of the coulomb integrals in the fluorine molecule is invariant with respect to the relative orientations of the lone pairs [1].

There is no significant difference between the spin polarized and the non-spin polarized localized orbitals. The only noticeable change is that the non-bonding orbitals for the beta-electrons become more localized on one atom, *i.e.* they have less bonding character. However, this is a small effect and it is not possible to give any qualitative interpretation of how the spin polarized treatment allows for electron correlation.

Sahni and Lorenzo [8] also considered the $^1\Delta_g$ state. However, the wave-function cannot be written as a single Slater determinant constructed from real orbitals. In fact, if real orbitals are used, the wavefunction is a sum of real and imaginary parts, each consisting of two determinants. It is not possible, therefore, to apply this method of localization to the ${}^1\Delta_g$ state.

## 4. Nitric Oxide

If real orbitals are used, the wavefunction for the ${}^2\Pi$ ground state can be written as the sum of two Slater determinants

$$\Psi = \frac{1}{\sqrt{2}} \{|1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^2 1\bar{\pi}^2 2\pi| + i|1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^2 1\bar{\pi}^2 2\bar{\pi}|\} .$$

Table 5. *Localized orbitals for nitric oxide*

| | $1S_N$ | $2S_N$ | $2p\sigma_N$ | $2p\pi_N$ | $2p\bar{\pi}_N$ | $1S_O$ | $2S_O$ | $2p\sigma_O$ | $2p\pi_O$ | $2p\bar{\pi}_O$ |
|---|---|---|---|---|---|---|---|---|---|---|
| A. *Energy localization* | | | | | | | | | | |
| (i) *Alpha-spins* | | | | | | | | | | |
| *i*N | 0.993 | -0.120 | 0.029 | 0.000 | 0.000 | 0.003 | 0.011 | -0.016 | 0.000 | 0.000 |
| *i*O | 0.003 | -0.013 | 0.008 | 0.000 | 0.000 | -0.991 | 0.130 | -0.024 | 0.000 | 0.000 |
| *nb*N | 0.093 | -0.676 | 0.266 | 0.719 | 0.000 | 0.014 | 0.089 | 0.095 | -0.075 | 0.000 |
| *nb*N | 0.093 | 0.676 | -0.266 | 0.719 | 0.000 | -0.014 | -0.089 | -0.095 | -0.075 | 0.000 |
| *nb*O | 0.016 | 0.110 | 0.145 | -0.075 | 0.000 | -0.099 | -0.687 | 0.277 | 0.719 | 0.000 |
| *nb*O | 0.016 | 0.110 | 0.145 | 0.075 | 0.000 | -0.099 | -0.687 | 0.277 | -0.719 | 0.000 |
| *b* | 0.000 | -0.133 | -0.333 | 0.000 | 0.370 | -0.011 | -0.193 | -0.383 | -0.000 | 0.531 |
| *b* | 0.000 | 0.133 | 0.333 | 0.000 | 0.370 | 0.011 | 0.193 | 0.383 | -0.000 | 0.531 |
| (ii) *Beta-spins* | | | | | | | | | | |
| *i*N | -0.993 | 0.116 | -0.028 | -0.000 | 0.000 | -0.003 | -0.010 | 0.015 | -0.000 | 0.000 |
| *i*O | 0.003 | 0.011 | -0.009 | 0.000 | 0.000 | 0.992 | -0.126 | 0.023 | 0.000 | 0.000 |
| *nb*N | -0.126 | -0.933 | 0.422 | -0.000 | 0.000 | 0.021 | 0.156 | 0.188 | -0.000 | 0.000 |
| *nb*O | -0.023 | -0.216 | -0.301 | -0.001 | 0.000 | 0.129 | 0.883 | -0.504 | -0.002 | 0.000 |
| *b* | 0.004 | 0.139 | 0.213 | 0.196 | -0.380 | 0.026 | 0.277 | 0.241 | 0.281 | -0.545 |
| *b* | -0.004 | -0.140 | -0.214 | 0.426 | -0.021 | -0.026 | -0.276 | -0.243 | 0.612 | -0.030 |
| *b* | 0.004 | 0.139 | 0.213 | 0.232 | 0.359 | 0.026 | 0.277 | 0.241 | 0.333 | 0.515 |
| B. *Uniform localization* | | | | | | | | | | |
| (i) *Alpha-spins* | | | | | | | | | | |
| *i*N | -1.001 | -0.005 | 0.005 | 0.000 | 0.000 | 0.000 | 0.014 | 0.015 | 0.000 | 0.000 |
| *i*O | 0.000 | 0.014 | 0.014 | 0.000 | 0.000 | -1.001 | -0.007 | 0.007 | 0.000 | 0.000 |
| *nb*N | 0.005 | 0.682 | -0.264 | 0.719 | 0.000 | -0.006 | -0.086 | -0.090 | -0.075 | 0.000 |
| *nb*N | 0.005 | 0.682 | -0.264 | -0.719 | 0.000 | -0.006 | -0.086 | -0.090 | 0.075 | 0.000 |
| *nb*O | 0.006 | 0.101 | 0.117 | 0.075 | 0.000 | -0.007 | -0.705 | 0.247 | -0.719 | 0.000 |
| *nb*O | 0.006 | 0.101 | 0.117 | -0.075 | 0.000 | -0.007 | -0.705 | 0.247 | 0.719 | 0.000 |
| *b* | -0.014 | 0.135 | 0.346 | 0.000 | 0.370 | -0.013 | 0.142 | 0.404 | 0.000 | 0.531 |
| *b* | -0.014 | 0.135 | 0.346 | 0.000 | -0.370 | -0.013 | 0.142 | 0.404 | 0.000 | -0.531 |
| (ii) *Beta-spins* | | | | | | | | | | |
| *bi*N | -1.001 | -0.005 | 0.005 | 0.000 | 0.000 | 0.000 | 0.014 | 0.015 | 0.000 | 0.000 |
| *i*O | 0.000 | 0.014 | 0.014 | 0.000 | 0.000 | -1.001 | -0.007 | 0.007 | 0.000 | 0.000 |
| *nb*N | 0.007 | 0.965 | -0.373 | 0.000 | 0.000 | -0.008 | -0.122 | -0.127 | 0.000 | 0.000 |
| *nb*O | 0.009 | 0.143 | 0.165 | 0.000 | 0.000 | -0.010 | -0.998 | 0.349 | 0.000 | 0.000 |
| *b* | -0.012 | 0.110 | 0.283 | 0.427 | 0.0 | -0.011 | 0.116 | 0.330 | 0.613 | 0.000 |
| *b* | -0.012 | 0.110 | 0.283 | -0.214 | -0.370 | -0.011 | 0.116 | 0.330 | -0.307 | -0.531 |
| *b* | -0.012 | 0.110 | 0.283 | -0.214 | 0.370 | -0.011 | 0.116 | 0.330 | -0.307 | 0.531 |

Table 6. *Transformation matrices — nitric oxide*

| | $1\sigma$ | $2\sigma$ | $3\sigma$ | $4\sigma$ | $5\sigma$ | $1\pi$ | $1\bar{\pi}$ | $2\pi$ |
|---|---|---|---|---|---|---|---|---|
| A. *Energy localization* | | | | | | | | |
| (i) *Alpha-spins* | | | | | | | | |
| *i*N | 0.000 | 0.990 | −0.070 | −0.106 | −0.057 | 0.000 | 0.000 | 0.000 |
| *i*O | 0.989 | 0.000 | 0.112 | −0.089 | 0.027 | 0.000 | 0.000 | 0.000 |
| *nb*N | 0.006 | −0.092 | −0.205 | −0.471 | −0.477 | 0.423 | 0.000 | 0.566 |
| *nb*N | 0.006 | 0.092 | 0.205 | 0.471 | 0.477 | 0.423 | 0.000 | 0.566 |
| *nb*O | 0.094 | 0.009 | −0.354 | 0.498 | −0.342 | 0.566 | 0.000 | −0.423 |
| *nb*O | 0.094 | 0.009 | −0.354 | 0.498 | −0.342 | −0.566 | 0.000 | 0.423 |
| *b* | 0.041 | −0.033 | −0.569 | −0.142 | 0.392 | −0.000 | 0.707 | 0.000 |
| *b* | 0.041 | 0.033 | 0.569 | 0.142 | −0.392 | −0.000 | 0.707 | 0.000 |
| (ii) *Beta-spins* | | | | | | | | |
| *i*N | −0.000 | −0.991 | 0.068 | 0.102 | 0.054 | −0.000 | 0.000 | |
| *i*O | 0.990 | −0.000 | −0.111 | 0.086 | −0.025 | −0.000 | 0.000 | |
| *nb*N | 0.014 | −0.121 | −0.205 | −0.644 | −0.727 | −0.000 | 0.000 | |
| *nb*O | 0.112 | −0.025 | 0.293 | −0.747 | 0.585 | −0.002 | 0.000 | |
| *b* | 0.050 | 0.031 | 0.534 | 0.055 | −0.203 | 0.374 | −0.726 | |
| *b* | −0.050 | −0.031 | −0.534 | −0.057 | 0.205 | 0.815 | −0.040 | |
| *b* | 0.050 | 0.031 | 0.534 | 0.055 | −0.203 | 0.443 | 0.686 | |
| B. *Uniform localization* | | | | | | | | |
| (i) *Alpha-spins* | | | | | | | | |
| *i*N | 0.000 | −1.000 | 0.025 | 0.008 | −0.009 | 0.000 | 0.000 | 0.000 |
| *i*O | −1.000 | 0.000 | 0.024 | 0.005 | −0.009 | 0.000 | 0.000 | 0.000 |
| *nb*N | 0.003 | 0.005 | 0.216 | 0.477 | 0.476 | 0.423 | 0.000 | 0.567 |
| *nb*N | 0.003 | 0.005 | 0.216 | 0.477 | 0.476 | −0.423 | 0.000 | −0.567 |
| *nb*O | −0.004 | −0.003 | −0.402 | 0.492 | −0.311 | −0.567 | 0.000 | 0.423 |
| *nb*O | −0.004 | −0.003 | −0.402 | 0.492 | −0.311 | 0.567 | 0.000 | −0.423 |
| *b* | 0.017 | 0.019 | 0.540 | 0.176 | −0.421 | 0.000 | 0.707 | 0.000 |
| *b* | 0.017 | 0.019 | 0.540 | 0.176 | −0.421 | 0.000 | −0.707 | 0.000 |
| (ii) *Beta-spins* | | | | | | | | |
| *i*N | 0.000 | −1.000 | 0.025 | 0.008 | −0.009 | 0.000 | 0.000 | |
| *i*O | −1.000 | 0.000 | 0.024 | 0.005 | −0.009 | 0.000 | 0.000 | |
| *nb*N | 0.005 | 0.007 | 0.305 | 0.674 | 0.673 | 0.000 | 0.000 | |
| *nb*N | −0.006 | −0.005 | −0.569 | 0.695 | −0.439 | 0.000 | 0.000 | |
| *b* | 0.014 | 0.015 | 0.044 | 0.143 | −0.344 | 0.817 | 0.000 | |
| *b* | 0.014 | 0.015 | 0.044 | 0.143 | −0.344 | −0.408 | −0.707 | |
| *b* | 0.014 | 0.015 | 0.044 | 0.143 | 0.344 | −0.408 | 0.707 | |

Although the localization methods are not strictly applicable to a wavefunction of this type, we thought it would be worthwhile to apply them to the real part.

The minimal basis set SCF – LCAO molecular orbitals of Brion, Moser, and Yamazaki [11] were used. The orthogonalized 2*s* orbitals were retained so that the integrals listed in their paper could be used.

The localized orbitals are in Table 5 and the transformation matrices in Table 6. As in the case of the oxygen molecule both methods of localization show the same general features.

For the electrons of alpha-spin there are inner shell orbitals for each atom, two "banana" bonding orbitals and two non-bonding orbitals on each atom. The non-bonding orbitals are in a plane perpendicular to that containing the bonding orbitals. The localized orbitals for the electrons of beta-spin are very similar to those for the oxygen molecule, namely one inner shell orbital and one non-bonding orbital on each atom and three "banana" bonding orbitals. This is also in good agreement with the formula of Linnett [5].

## 5. Conclusion

The main conclusion of this work is that localized orbitals can be derived for odd electron molecules by considering separately the orbitals containing alpha- and beta-electrons. The results for the oxygen molecule and nitric oxide are in good agreement with the formulae suggested by Linnett [5].

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