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Deformed Hartree-Fock solutions for atoms. III. Convergent iterative process and results for O^{--}

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We present a systematic study of self-consistent symmetries (SCS) for the ten-electron atom O^{--} in an $s+p$ basis. The investigation of each SCS required a detailed study of the character of the iterative process. Convergency is ensured by a minimum-energy selection principle. Six deformed Hartree-Fock solutions for O^{--} have been obtained.

I. INTRODUCTION

The quantum theory of atomic structure gives the quantum chemist either central-field Hartree-Fock-Roothaan functions (e.g., the ^1S state in the $1s^2 2s^2 2p^2$ configuration), where, at most, N radial functions are associated with N electrons; or sophisticated atomic wave functions, such as the multiconfigurational self-consistent-field (SCF) function, or perturbation expansions based on the central-field approximation, and in these two cases more than N spin orbitals are associated to N electrons. The latter cannot be used in the quantum theory of molecular structure, and on the other hand, the "simple" central-field picture needs to be either distorted or, in hopeless cases, considered as merely giving some privileged basis (in a mathematical meaning) for molecular calculations. For instance, in semiempirical calculations, valence states of atoms are built in at the beginning of the molecular electronic structure calculation, while in molecular *ab initio* calculations, atomic orbitals provide no more than a mathematical basis for vectorial spaces. Clearly, there is a gap between the theory of isolated atoms and the theory of electronic structure of molecules: A knowledge of the isolated atom spectroscopic states does not provide an understanding of the valence properties of the same atom.

On the other hand, atomic spectroscopists like to see atoms as "spherical"; indeed, the electronic density in any spectroscopic state is spherically symmetric. This is a trivial statement.[1] "Atoms are spherical" is a more meaningful statement. By it, it is meant that both the independent-particle model and the central-field approximation work well, that is, spectroscopic states calculated in the model and under this approximation have energy accurate enough to compare with experiment. If some failure, for instance, in transition probabilities calculations, or in frequency ratios occurs, one has to introduce "correlation," that is a correction to the independent-particle model, generally not to the central-field approximation.

We are not convinced that the building up of some isotropic Hartree-Fock field gives a satisfactory picture of the physical atom. We prefer to think that the one-particle field is a central one, *plus* anisotropies necessary to understand the bonding properties of the atom. With deformed Hartree-Fock wave functions, N spin orbitals are associated with N electrons, and furthermore, each deformed state is "sophisticated" because it is a superposition of stationary states each of them being described by a multideterminantal wave function. Our present hope is that some deformed Hartree-Fock solutions will emerge giving, first, representations of spectroscopic states equivalent to the correlated central field one, and second, a better understanding of the valence properties of atoms.

The determination of atomic deformed Hartree-Fock solutions is not easy anyway. Here we present results about the system O^{--} (doubly negative oxygen ion) more complete than those previously given.[2] In future work results about carbon in ground-state configuration will be given. The present paper will deal in Sec. II with the self-consistent symmetries in a ten-electron atom, especially in an $s+p$ basis; in Sec. III a study of the iterative process is presented, and in Secs. IV and V a description will be found together with some comments about six Hartree-Fock solutions obtained for O^{--} in an $s+p$ basis.

II. SUMMARY OF RELEVANT HARTREE-FOCK THEORY AND SELF-CONSISTENT SYMMETRIES FOR O^{--}

The Hamiltonian of our system is

$$H=\sum_{\mu=1}^{N} h(\mu)+\tfrac{1}{2}\sum_{\mu\nu}{}' \frac{1}{|\vec{r}_\mu-\vec{r}_\nu|}\ ,$$

where $h(\mu)=-\tfrac{1}{2}\nabla^2(\mu)-Z/r_\mu$. The spin orbitals

ϕ_i in the Slater determinant

$$\phi = |\phi_1 \cdots \phi_N|$$

are assumed to be orthonormal without any loss of generality, and no variational constraint[3] is needed to keep them so, when used in the variational principle

$$\langle \delta\phi | H | \phi \rangle = 0 \quad \text{at } \phi = \phi_0 .$$

The last equation associates to H and to ϕ a Fock Hamiltonian

$$F(\mu) = h(\mu) + \sum_{i=1}^{N} \int \phi_i^*(\nu) \frac{1 - P_{\mu\nu}}{|\vec{r}_\mu - \vec{r}_\nu|} \phi_i(\nu)\, d\tau_\nu ,$$

where $P_{\mu\nu}$ permutes space and spin coordinates of particles μ and ν. Let

$$V(\mu) = \sum_{i=1}^{N} \langle \phi_i | V_A | \phi_i \rangle \equiv F(\mu) - h(\mu)$$

be the antisymmetrized Hartree-Fock potential. The variational principle is satisfied at $\phi = \phi_0$ when the spin-orbitals ϕ_{0i} are solutions of the nonlinear equations

$$F_0 \phi_{0i} = \sum_{j=1}^{N} \phi_{0j} \epsilon_{ji} , \quad i = 1, \ldots, N.$$

Canonical spin orbitals are defined by

$$F_0 \phi_{0i}^{\text{can}} = \epsilon_i \phi_{0i}^{\text{can}} .$$

In both cases, F_0 is that Fock Hamiltonian which is built upon N spin orbitals ϕ_{0i} satisfying either nonlinear equation.

Generally speaking, because of nonlinearity, there are several solutions ϕ satisfying $\langle \delta\phi | H | \phi \rangle = 0$. Let ϕ_0 and ϕ_0' be two variational solutions, they define two occupied subspaces

$$\phi_{0i} ,\ i = 1, \ldots, N \ \text{and}\ \phi_{0i}' ,\ i = 1, \ldots, N,$$

neither orthogonal nor equivalent to each other, and two virtual subspaces. So, the nonlinear system

$$F\phi_i = \sum_j \phi_j \epsilon_{ji} , \quad j, i = 1, \ldots, N,$$

will have at least two solutions satisfying it. The first one is

$$\left(h + \sum_{j=1}^{N} \langle \phi_{0j} | V_A | \phi_{0j} \rangle \right) \phi_{0i} = \sum_{j=1}^{N} \phi_{0j} \epsilon_{ji} ,$$

and the other one is

$$\left(h + \sum_{j=1}^{N} \langle \phi_{0j}' | V_A | \phi_{0j}' \rangle \right) \phi_{0i}' = \sum_{j=1}^{N} \phi_{0j}' \eta_{ji} .$$

The iterative method has been used here. Let us remember that, having at the iteration number n an orthonormalized set of N spin orbitals

$$\phi_i^{(n)} , \quad i = 1, \ldots, N,$$

one builds up a Hamiltonian

$$F^{(n)} = h + V^{(n)}$$

and solves for canonical eigenfunctions $\phi_i^{(n+1)}$,

$$F^{(n)} \phi_i^{(n+1)} = \epsilon_i^{(n+1)} \phi_i^{(n+1)} ,$$

so that we have now a complete orthonormalized set $(\phi_a^{(n+1)} ,\ a = 1, 2, \ldots)$. One chooses (cf. Sec. III) in that set N spin orbitals (eventually) relabeled from 1 to N and builds again an equation

$$F^{(n+1)} = h + \sum_{i=1}^{N} \langle \phi_i^{(n+1)} | V_A | \phi_i^{(n+1)} \rangle .$$

We have now come back to the beginning of the cycle. When the process converges (cf. Sec. III), one obtains either the ϕ_{0i} or the ϕ_{0i}' .

One can understand how two (or more) determinants ϕ_0 and ϕ_0' may be distinct variational solutions on considering their symmetry properties. Let G be the invariance group of the total Hamiltonian H; then it is sufficient that ϕ_0 and ϕ_0' be unchanged by two distinct subsets E and E' belonging to G such as, for instance,

$$E' \subset E \subset G;$$

in effect, one is then able to find some symmetry transformation S leaving ϕ_0 unchanged,

$$S\phi_0 = \lambda\phi_0 ,$$

but eventually not ϕ_0'. If we suppose that E and E' differ by no more than one S, we see that ϕ_0 might be formed by varying a determinant belonging to the family ϕ' (of which ϕ_0' is a particular one), subject to the constraint that ϕ' would in addition be invariant by operating with S. So, we conclude that a variational solution with higher symmetry ϕ_0, also leads to a higher energy[4]

$$E(\phi_0) \geq E(\phi_0') .$$

Moreover, if S does not commute with the transformations of the set E', ϕ_0 will be distinct from ϕ_0'. In the case when S commutes with every member of E', ϕ_0 either will or will not be different from ϕ_0'.

Subsets of mutually commuting symmetry transformations may be found *a priori;* to each subset one may associate an invariant Slater determinant. We have given more details about self-consistent symmetries elsewhere[5]; here we shall illustrate the process in the case of the ten-electron system O^{--} studied in a Slater-orbital basis limited to s and p species.

Having the origin of the system of coordinates at the infinite mass nucleus, the Hamiltonian H is unchanged by spin and space rotations and invariant by time reversal[6] and parity.

Here we might mention that our spin-independent Hamiltonian allows a distinction between time reversal on spins only and time reversal on space functions only. However, as a result of the Pauli principle, which couples spin and space functions, we have to operate simultaneously on spin and space coordinates by time reversal; so that, for instance, we have

$$T[\alpha R(\rho)Y_{lm}(\Omega)] = (-1)^{l-m}\beta R^*(\rho)\, Y_{l-m}(\Omega),$$

where ρ and Ω $(=\theta, \varphi)$ are spherical coordinates.

Coming back to the system O^{--}, we shall not include parity-mixed determinants in our table of self-consistent symmetries. The reason for this is that any attempt to obtain a parity-mixed Hartree-Fock solution has in fact given a parity-defined solution. Table I is arranged first with respect to spin rotation properties of a determinant, giving four species; in each species a determinant either may or may not have axial symmetry, thus giving two or more varieties; and in each variety a determinant either may or may not be time-reversal invariant, which gives two or more families (the number of varieties may be great, according to the value M taken by the projection L_z of the total angular momentum). However, as presumably Hartree-Fock varieties having M defined and nonzero will lie high in energy, we have restricted our investigation on O^{--} to two varieties, namely, the M nondefined, and the $M=0$ one.

III. CHARACTER OF ITERATIVE PROCESS

In principle, to each of the self-consistent symmetries there corresponds a Fock Hamiltonian. In practice, one does not obtain all of them, first because of lower-energy solution, say, our previous ϕ_0' does not exist when it collapses with ϕ_0 (accidental degeneracy is disregarded as highly unprobable); second, because the iterative process does not always converge. Previous studies of the iterative process[7-10] have shown that the direct minimization of the energy functional $E(\phi)$ generally leads to more solutions than by using the iterative process. Koutecký and Bonačić found that the solutions in excess cannot be reached by the usual iterative process.[8,9] Harvey and Jensen[7] showed that in a two-electron problem, the position of the (noninteracting) triplet state influences the iterative solution for the closed-shell singlet, so that in some cases the process diverges. Stanton,[10] on the other hand, has been able to give an upper limit to the number of Hartree-Fock solutions in N orbital basis functions. However, the previous studies do not take into account the effect of the imposed symmetry restrictions on the character of convergency; in addition, they do not consider other roads leading

TABLE I. Self-consistent symmetries for the ground state of O^{--} in an s-p basis. The sign ~ indicates undefined values of observables.

Species	S^2	S_z	L^2	L_z	Radial part of atomic orbitals	$T\,\Delta$
Species 1: complete shell determinant $1s^2 2s^2 2p^6$	0	0	0	0	always real	$=\Delta$
Species 2: closed shells $1s^2 2s^2 2p_0^2 (2p'_{+1})(2p''_{-1})^2$	0	0	~	0	real and $R(p'_{+1}) = R(p''_{-1})$	$=\Delta$
	0	0	~	0	complex but $R^*(p'_{+1}) = R(p''_{-1})$ and $R^*(p_0) = R(p_0)$	$=\Delta$
	0	0	~	0	complex	$\neq\Delta$
	0	0	~	~	any	$\neq\Delta$
Species 3: unrestricted Hartree-Fock determinant $\lvert 1s\alpha\, 1s'\beta\, 2s\alpha\, 2s'\beta\, p_0\alpha\, p_0'\beta\, q_{+1}\alpha\, q'_{+1}\beta\, r_{-1}\alpha\, r'_{-1}\beta\rvert$	~	0	~	0	real or complex but $1s' = 1s^*$, $2s' = 2s^*$, $p' = p^*$, $r' = q^*$, and $q' = r^*$	$=\Delta$
	~	0	~	0	any	$\neq\Delta$
$\lvert 1s\alpha\, 1s'\beta\, 2s\alpha\, 2s'\beta\, p\alpha\, p'\beta\, q\alpha\, q'\beta\, r\alpha\, r'\beta\rvert$	~	0	~	~	any	$\neq\Delta$
Species 4: general Hartree-Fock $\lvert \phi_1\phi_2\phi_3\phi_4\phi_5\phi_6\phi_7\phi_8\phi_9\phi_{10}\rvert$ with ϕ_i $(i=1$ to $4) = s_i\alpha + s_i'\beta$	~	~	~	0	any	$\neq\Delta$
ϕ_i $(i=5$ to $10) = p_i\alpha + p_i'\beta$	~	~	~	~	any	$\neq\Delta$

to convergency.

Two ingredients influence the issue of the iterative process. The first one is the choice one makes for the ten first spin-orbitals ($\phi_i^{(0)}$, $i=1,\ldots,10$) at zeroth iteration. One can choose them with definite symmetry species according to Table I. But apart from a subtle feeling of these things, one cannot assert that the $\phi_i^{(0)}$'s are chosen according to an *aufbau* principle.[11] The second ingredient is related to the building of $F^{(n)}$, the Fock operator at iteration number $n+1$. One has to choose ten spin orbitals, and therefore label them from 1 to 10. One may think that the principle of the choice may be once and for all adopted, leading to eventually different choices for iteration step n and iteration step $n+1$. Suppose the canonical spin-orbitals obtained at step n are arranged by order of increasing energy; let $(p_1, p_2, \ldots, p_{10})$ be ten ones selected according to some principle, at step $n+1$; the same principle applied to the selection of ten spin orbitals at step $n+2$ may lead to a different set $(p_1', p_2', \ldots, p_{10}')$, or to the same set $(p_1, p_2, \ldots, p_{10})$; for instance, the standard choice $(1, 2, \ldots, 10)$ stems from an *aufbau* principle, and is a constant choice along the iterative process. One knows that the *aufbau* principle may lead to oscillation or to divergency. One knows techniques such as a mixing of Fock potentials

$$(V')^{(n)} = \lambda V^{(n)} + \mu V^{(n-1)}$$

or a mixing of spin-orbitals

$$(\phi_i')^{(n)} = \lambda\phi_i^{(n)} + \mu\phi_j^{(n-1)},$$

where $\phi_j^{(n-1)}$ is that spin-orbital at step $n-1$, which together has the same symmetry as $\phi_i^{(n)}$ and satisfies the *aufbau* principle. Even then the process may diverge; in fact, oscillations are slowed down, and disappear for some (λ, μ), but the speed of the process is slowed too.

The *aufbau* principle is based on two approximations. First, the neglect of the interaction terms in the expression for the energy of a determinantal solution. At convergency, one has

$$E = \sum_{i=1}^{10} \epsilon_i - \tfrac{1}{2}\sum_{ij} (V_{ij,ij} - V_{ij,ji}) \qquad \text{where } \epsilon_1 \leqslant \epsilon_2 \leqslant \cdots \leqslant \epsilon_{10},$$

so that $E \sim \sum_{i=1}^{10} \epsilon_i$, justifying the *aufbau* principle. However, at iteration step $n-1$, the total energy is not expressed in terms of the spin-orbital energies ϵ_i at convergency, so that one may see that far from convergency, the *aufbau* principle may not be convenient. Second, the usefulness of the *aufbau* principle comes from the expression of the second variation of a Hartree-Fock solution (cf. Adams[12]), which has to be positive if the solution is stable.[13] Apart from interaction terms, here too the second variation is

$$E^{(2)} \sim \sum_{i=1}^{10} \sum_{m>10} (\epsilon_m - \epsilon_i)\,|C_{mi}|^2,$$

where the C_{mi} are complex coefficients. One sees that the approximate value of $E^{(2)}$ will be positive if $\epsilon_m > \epsilon_i$, in their respective labeling range, that is when all occupied spin orbitals have lower energy than any empty one. The *aufbau* principle will presumably lead to a more stable or minimum energy solution.

However, the two approximate properties of Hartree-Fock solutions are properties at *convergency,* and indicate only that one has good reasons to think that Hartree-Fock solutions satisfy the *aufbau* principle. They say nothing about the character of convergence of the iterative process.

Here we have based the selection of occupied orbitals to occur in $F^{(n)}$, the Fock Hamiltonian at iteration step $n+1$, on the following principle: Select two or more [up to Col $(10, N)$] sets of 10 spin-orbitals $\phi_i^{(n)}$, then compute the total energy associated with each of the Slater determinants built on the successive sets. One then obtains values $E[\phi_1^{(n)}], E[\phi_2^{(n)}], \ldots$. Compare these values and take for an occupied set at step $n+1$ that set which is associated with the lowest value $E[\phi_{\text{min}}^{(n)}]$. This applies to the computation of the ground Hartree-Fock state belonging to each self-consistent symmetry. The choice so operated is not uniform, although the principle of the choice is the same at each iteration step.

The operation of such a minimum energy selection principle resulted in elimination of divergencies or oscillations of the iterative process in all cases investigated here, that is the process always converged.

It is interesting to note that at convergency all our Fock operators have satisfied the *aufbau* principle. Having this result in mind, one can say that the minimum energy selection principle is a method used to find a starting point convenient to apply the *aufbau* principle. Let $C^{(0)}$ be the standard choice $(1, 2, \ldots, 10)$ and $C^{(p)}$ $(p \neq 0)$ a nonstandard one; the minimum energy selection principle gives the following choices:

$$\begin{array}{lcccccccc} \text{Iteration} & 0 & 1 & 2 & \cdots & n & n+1 & \cdots & \text{Convergency} \\ \text{Choice} & C^{(p)} & C^{(p')} & C^{(p'')} & \cdots & C^{(q)} & C^{(0)} & \cdots & C^{(0)} \end{array},$$

TABLE II. Exponents for Slater-type orbitals (Ref. 14). In the third column is found a more convenient notation for s and p basis functions.

$1s^{\mathrm{I}}$	12.757 721	s^1	$2p^{\mathrm{I}}$	4.995 795 4	p^1
$1s^{\mathrm{II}}$	7.093 308 2	s^2	$2p^{\mathrm{II}}$	2.449 378 2	p^2
$3s$	8.970 814 1	s^3	$2p^{\mathrm{III}}$	1.042 114 5	p^3
$2s^{\mathrm{I}}$	2.753 601 9	s^4	$2p^{\mathrm{IV}}$	0.165 20	p^4
$2s^{\mathrm{II}}$	1.526 654 9	s^5			

TABLE IV. Closed-shell solution (a slightly different solution, owing to slightly different STO basis, has been given in Ref. 2), $|1s\,\overline{1s}\,2s\,\overline{2s}\,2p_0\overline{2p}_0 2p_-\overline{2p}_- 2p'_+\overline{2p}'_+|$ with intrinsic axial symmetry. Top entries are orbital energies. All coefficients real. Total energy is −74.601 246 a.u.

s^μ	−20.426 80	−0.996 745
1	0.077 937	0.003 181
2	0.954 696	−0.267 406
3	−0.033 446	−0.033 356
4	0.002 955	0.741 076
5	−0.000 300	0.363 784

$p^\nu_{0,-}$	−0.310 151	p^ν_+	+0.077 022
1	0.092 340	1	0.027 983
2	0.637 117	2	0.180 934
3	0.397 492	3	0.180 692
4	−0.013 316	4	0.906 882

so that, if one had known in advance the occupied spin orbitals at iteration step $n+1$, the *aufbau* principle would have lead to convergency.

In practice the requirements concerning the symmetry properties of occupied spin orbitals complicate the programming of convergence procedure. The over-all symmetry of the Slater determinant has to be conserved from one iteration to the following one. For instance, let us suppose that we are seeking for a solution with $S_z=0$ and $L_z=1$ for some ten-electron atomic system. The ten occupied spin-orbital sets, the energies of which are compared, will have to be made up of five spin orbitals with spin $\frac{1}{2}$, five with spin $-\frac{1}{2}$, and values $m_1, m_2, \ldots, m_{10}$ of L_z such that

$$\sum_{i=1}^{10} m_i = 1 .$$

Our program is written in such a manner that, in pathological cases, one can choose the occupied set according to the minimum energy selection principle, until some constant choice (usually the standard one) emerges, and then one flips to the simpler convergency road (usually the *aufbau* principle).

IV. RESULTS

We have studied the ten-electron atomic system O^{--} for which we know[2] that a spherical Hartree-Fock solution exists in the space of the ground-state configuration. The Fock Hamiltonian can then have many self-consistent symmetries up to the spherical one. We are given a basis of five s-type and four p-type Slater orbitals, here they are optimized with respect to the spherical solution set obtained by S. Huzinaga[14] (see Table II). Three angular functions and two spin functions are associated with each $2p$ radial Slater orbital, so that our basis is a 34-dimensional basis

$$10\ s\ \text{type}\ \begin{cases} s^\mu\alpha, & \mu=1,\ldots,5 \\ s^\mu\beta, & \mu=1,\ldots,5, \end{cases}$$

$$24\ p\ \text{type}\ \begin{cases} p^\nu_m\alpha, \\ p^\nu_m\beta, \end{cases} \quad m=-1,0,1;\ \nu=1,\ldots,4 \quad .$$

The general form of a spin orbital is

$$\phi_i = a_i\alpha + b_i\beta .$$

The a_i and b_i are given by the expansions

$$a_i = \sum_{\mu=1}^{5} s^\mu a_{\mu i} + \sum_{\nu=1}^{4}\ \sum_{m=-1}^{+1} p^\nu_m a^m_{\nu i} ,$$

$$b_i = \sum_{\mu=1}^{5} s^\mu b_{\mu i} + \sum_{\mu=1}^{4}\ \sum_{m=-1}^{+1} p^\nu_m b^m_{\nu i} ,$$

TABLE III. The Huzinaga central field solution $\phi = |1s\,\overline{1s}\,2s\,\overline{2s}\,2p_-\overline{2p}_- 2p_0\overline{2p}_0 2p_+ 2\overline{p}_+|$; all coefficients a_{ri} and b_{ri} are real. Entries on the top line are the energies of the two $1s$, two $2s$, and six $2p$ occupied spin orbitals in ϕ. Total energy is −74.507 127 a.u.

s^μ	−20.126 278 a.u.	−0.704 458 59 a.u.	p^ν	+0.065 692 242
1	0.077 91	0.004 17	1	0.084 75
2	0.954 34	−0.263 50	2	0.481 27
3	−0.033 57	−0.026 51	3	0.467 02
4	0.002 81	0.693 43	4	0.341 92
5	−0.000 11	0.409 04		

TABLE V. Closed-shell solution [stability conditions and properties of closed-shell solutions will appear in a paper by J. Paldus, R. F. Prat, and J. Cizek (to be published), paper II of the series], $|1s\,\overline{1s}\,2s\,\overline{2s}\,2p_+\,\overline{2p}_+\,2p'_0\,\overline{2p}'_0\,2p''_{-1}\,\overline{2p}''_{-1}|$. Top entries are orbital energies for $1s$, $2s$, $2p_+$, $2p'_0$, and $2p''_-$ spin-orbital pairs. All coefficients are real but the solution is not T invariant. Total energy is −74.635 119 a.u.

s^μ	−20.486 31	−1.057 46
1	0.077 95	0.002 96
2	0.954 64	−0.268 06
3	−0.033 40	−0.034 76
4	0.003 01	0.750 17
5	−0.000 35	0.355 09

p_+^ν	−0.415 72	p_0^ν	−0.373 33	p_-^ν	+0.073 63
1	0.090 70	1	0.091 56	1	0.016 00
2	0.672 91	2	0.650 67	2	0.114 97
3	0.356 75	3	0.382 38	3	0.098 77
4	−0.014 56	4	−0.014 29	4	0.960 94

with complex expansion coefficients $a_{\mu i}$, $b_{\mu i}$, $a^m_{\nu i}$, and $b^m_{\nu i}$. As previously stated, any attempt to obtain a parity-mixed (s- and p-mixed) solution has failed, so that our results may be reproduced by assuming that either $a_{\mu i}$ and $b_{\mu i}$, or $a_{\nu i}$ and $b_{\nu i}$ vanishes.

We have finally obtained six Hartree-Fock solutions. This means that (as far as our investigation is concerned) the atomic system O^{--} possesses six ground-state self-consistent symmetries. In Table III, the Huzinaga central-field solution appears, which is both highest in symmetry and highest in energy. We have reproduced here (Table IV) the intrinsic axially symmetrical solution which appeared in a previous paper[2] (using the slightly different orbital set of Clementi). In Table V a low-energy solution is presented, and additional calculations related to the solution of Table V are presented in Table VI. In addition, Tables VII–IX are three other low-energy solutions.

V. DISCUSSION

In Tables III–IX we have given six ground-state Hartree-Fock solutions for the system O^{--} studied in a limited s-p basis. We note that the calculations have been restricted to the ground-state configuration; in less pathological systems this restriction would certainly be not too serious, but for O^{--} one can think that $d, f, \ldots,$ basis functions would be relevant too. However, if our task is the best calculation for O^{--}, this will consume too much computer time and memory. In the framework of an s-p calculation, one might improve the quantitative result by optimization of the basis set for each solution, again we do not claim the best quantitative results. Our problem was to obtain the largest possible number of ground-state Hartree-Fock solutions as predicted in Table I of self-consistent symmetries.

For instance (cf. Table IX), when one seeks for a determinantal solution with mixed spin, complex radial functions, and neither definite parity nor specified l_z-value orbitals, one is led by the iterative procedure with minimum energy selection principle to the solution in Table IX, where spins are no longer mixed and parity is conserved. In this respect, we note that we do not repeat any previous solution (Tables III–VIII), although we might. In fact, each self-consistent symmetry is unstable unless the lowest energy one is reached. As the Fock potential corresponding to the last case in Table I is not constrained to have a specified symmetry, one sees that if, near the Table V solution, the Fock Hamiltonian is only nearly a

TABLE VI. Evolution of the Table V solution on lowering of $\zeta(p^4)$. (a) Total energy, and (b) $2p_+$ and $2p'_0$ orbital energies. In addition, the $2p''_-$ orbital energy goes to zero, while the weight of p^4 increases from 0.960 94 to 1.

				Total energy			
O^{--}	−74.635 119	−74.663 080	−74.688 621	−74.710 737	−74.714 642	−74.716 149	−74.716 449
$O(^1D)$	−74.717 009	0.716 707	0.716 605	0.716 594	0.716 594	0.716 594	0.716 594
ζ^4	0.165 20	0.115 20	0.065 20	0.015 20	0.005 20	0.001 20	0.000 40
				$2p_+$ and $2p'_0$ orbital energies			
$2p_+(O^{--})$	−0.415 719	−0.485 309	−0.555 122	−0.616 637	−0.626 776	−0.630 778	−0.631 578
$2p_+(O,{}^1D)$	−0.631 759	−0.631 913	−0.631 968	−0.631 974	−0.631 974	−0.631 974	−0.631 974
$2p_0(O^{--})$	−0.373 329	−0.441 591	−0.510 361	−0.571 340	−0.581 473	−0.585 474	−0.586 274
$2p_0(O,{}^1D)$	−0.586 481	−0.586 617	−0.586 665	−0.586 670	−0.586 670	−0.586 670	−0.586 670
ζ^4	0.165 20	0.115 20	0.065 20	0.015 20	0.005 20	0.001 20	0.000 40

TABLE VII. UHF solution $|\overline{1s}\,1s'\,\overline{2s}\,2s'\,\overline{2p}_{+1}\,\overline{2p}_{-1}\,\overline{2p'_0}\,2p''_0\,2p'''_+\,2p''''_-|$. Top entries are orbital energies. Expansion coefficients are real but the solution is not time-reversal invariant. Spin orbitals are arranged by order of increasing energy both in the UHF determinant and in the Table. Total energy is −74.698 322 a.u.

s^μ	−20.144 12	−20.104 69	−0.826 015	−0.653 063		
1	0.078 18	0.077 78	0.003 49	0.004 30		
2	0.953 43	0.955 60	−0.265 79	−0.257 78		
3	−0.032 60	−0.034 09	−0.030 14	−0.023 57		
4	0.004 29	0.001 94	0.714 36	0.658 59		
5	−0.000 51	0.000 01	0.389 43	0.442 23		
p^ν	−0.106 39	−0.106 39	−0.066 36	−0.003 08	−0.000 74	+0.092 55
1	0.091 51	0.091 51	0.092 74	0.093 19	0.093 09	−0.007 64
2	0.590 02	0.590 02	0.565 73	0.503 05	0.500 51	0.036 19
3	0.450 75	0.450 75	0.475 54	0.534 78	0.536 80	−0.080 46
4	−0.003 78	−0.003 81	0.006 11	0.054 77	0.058 62	1.009 46

closed-shell one, the "open shell part" will make the process to slip toward the lower UHF Table VII solution, which is again unstable with respect to spin mixing, for example.

Another point to be made is about the ordering of Hartree-Fock total energies. One may understand why the solution in Table VII is higher in energy than the one in Table IX (additional reality constraint for radial functions), but one has to accept that the solution given in Table IX is below that in Table VIII, in other words, that here some hierarchy operates between self-consistent sym-

TABLE VIII. General Hartree-Fock solution $\phi = |\phi_1\phi_2\cdots\phi_{10}|$. Top entries are spin-orbital energies. Expansion coefficients a_{ri} and b_{ri} are real. Not T invariant. Total energy is −74.722 098 a.u. (a) s symmetry, and (b) p symmetry.

			s symmetry			
s^μ	−20.544 17	−20.463 54	−1.259 97	−0.915 18		
1α	0.078 40	0.000 01	0.002 21	0.0		
2α	0.952 25	0.000 16	−0.275 29	−0.000 03		
3α	−0.031 75	−0.000 01	−0.040 70	0.0		
4α	0.005 57	0.0	0.799 64	0.000 06		
5α	−0.001 01	0.0	0.306 92	0.000 06		
1β	−0.000 01	0.077 56	0.0	0.003 50		
2β	−0.000 16	0.956 74	0.000 03	−0.259 46		
3β	0.000 01	−0.034 87	0.000 01	−0.029 09		
4β	0.0	0.000 76	−0.000 10	0.695 17		
5β	0.0	0.000 15	−0.000 02	0.408 00		
			p symmetry			
p^ν	−0.546 66	−0.503 23	−0.503 23	−0.344 76	+0.066 49	+0.066 81
1α	0.088 32	0.089 20	0.089 20	0.000 01	−0.000 09	−0.000 10
2α	0.723 77	0.706 43	0.706 43	0.000 07	−0.000 12	−0.000 12
3α	0.296 50	0.317 30	0.317 30	0.000 08	−0.000 75	−0.000 79
4α	−0.014 40	−0.014 66	−0.014 66	0.000 01	0.013 22	0.013 11
1β	−0.0	−0.000 01	0.0	0.090 82	0.002 50	0.002 35
2β	−0.000 08	−0.000 11	−0.000 08	0.608 95	0.045 08	0.045 72
3β	0.000 02	−0.000 04	0.000 02	0.430 95	0.000 70	−0.000 67
4β	0.000 09	0.0	0.000 11	−0.013 55	0.997 44	0.997 65
m	0	−1	+1	−1	0	+1

metries (remember that the solution in Table VIII has been reached although complex radial functions were allowed). Let us now review each solution separately.

Table III is the complete shell ^1S solution; the Fock Hamiltonian has spherical symmetry, that is the symmetry properties of the total Hamiltonian. The solution coincides with the standard radial Hartree-Fock solution for O^{--}. Convergence of the iterative procedure on this state is difficult. The singlet stability matrix[15] has two negative eigenvalues, indicating that two closed-shell determinants exist with total energy below −74.507 a.u. One then finds solutions for Tables IV and V.

The solution given in Table IV has already been described.[2] We just emphasize that first, it is an axially symmetric solution in the sense commonly used in nuclear physics. That is, it is invariant under rotation about the z-quantization axis, but on the other hand, it is an intrinsic axially symmetric solution because the Fock Hamiltonian is invariant under the real orthogonal transforma-

TABLE IX. Lowest general Hartree-Fock solution, really an UHF one. Top entries are orbital energies. Expansion coefficients are complex and presented in the form "real part ( ) imaginary part." Not T invariant. Total energy is −74.722 770 a.u. (a) s symmetry, (b) $p\beta$ symmetry, (c) $p\alpha$ symmetry.

s symmetry

s^μ	−20.544 15		−20.463 70		−1.259 77		−0.915 40	
1	0.078 40	0.0	0.077 56	0.0	0.002 21	0.0	0.003 50	0.0
2	0.952 26	0.0	0.956 74	0.0	−0.275 27	0.0	−0.259 50	0.0
3	−0.031 76	0.0	−0.034 86	0.0	−0.040 69	0.0	−0.029 12	0.0
4	0.005 56	0.0	0.000 77	0.0	0.799 49	0.0	0.695 43	0.0
5	−0.001 01	0.0	0.000 15	0.0	0.307 07	0.0	0.407 75	0.0
Spin	β		α		β		α	

$p\beta$ symmetry

m	p^ν	−0.546 62		−0.546 41		−0.459 77	
−1	1	0.020 52	0.031 91	0.027 60	0.053 59	0.053 29	0.000 03
	2	0.168 12	0.261 47	0.226 15	0.439 08	0.406 61	0.000 23
	3	0.068 89	0.107 14	0.092 70	0.179 99	0.200 82	0.000 11
	4	−0.003 35	−0.005 20	−0.004 50	−0.008 74	−0.008 71	0.0
0	1	0.070 16	0.0	−0.010 21	0.020 72	−0.044 31	0.021 85
	2	0.574 91	0.0	−0.083 68	0.169 74	−0.338 12	0.166 69
	3	0.235 57	0.0	−0.034 30	0.069 58	−0.166 99	0.082 33
	4	−0.011 44	0.0	0.001 67	−0.003 38	0.007 24	−0.003 57
+1	1	−0.020 52	0.031 91	0.059 32	−0.010 74	−0.032 43	0.042 29
	2	−0.168 13	0.261 47	0.485 99	−0.088 00	−0.247 42	0.322 66
	3	−0.068 89	0.107 14	0.199 22	−0.036 07	−0.122 20	0.159 36
	4	0.003 35	−0.005 20	−0.009 67	0.001 75	0.005 30	−0.006 91

$p\alpha$ symmetry

m	p^ν	−0.346 35		+0.066 50		+0.066 50	
−1	1	0.056 67	−0.000 01	0.000 58	0.000 90	0.000 68	0.001 40
	2	0.380 52	−0.000 09	0.010 48	0.016 29	0.013 03	0.026 33
	3	0.267 80	−0.000 06	0.000 16	0.000 24	−0.000 20	−0.000 14
	4	−0.008 54	0.0	0.231 93	0.360 27	0.294 89	0.591 45
0	1	−0.043 89	0.023 50	0.001 98	0.0	−0.000 17	0.000 64
	2	−0.294 67	0.157 82	0.035 82	−0.000 02	−0.004 15	−0.011 10
	3	−0.207 34	0.111 07	0.000 53	0.0	0.000 45	0.000 41
	4	0.006 62	−0.003 54	0.792 40	−0.000 45	−0.100 62	0.241 22
+1	1	−0.030 86	0.040 22	−0.000 58	0.000 90	0.001 81	−0.000 29
	2	−0.207 24	0.270 07	−0.010 47	0.016 30	0.031 67	−0.005 23
	3	−0.145 80	0.190 00	−0.000 15	0.006 24	0.001 04	−0.000 07
	4	0.004 66	−0.006 07	−0.231 57	0.360 51	0.690 34	−0.115 89

tions (in the five-dimensional space spanned by the occupied orbitals), which are induced in that space by rotations in configuration space about the axis defined by the positive energy last occupied orbital.

In Table V is shown a closed-shell axially symmetric solution with no intrinsic axis. The Fock Hamiltonian (that is the electronic-density) is invariant by inversion at the origin and rotations of 180° about each (mutually orthogonal) axis defined by each occupied $2p$ orbital, that is, briefly, the symmetry group of the ellipsoid. In addition, the Fock Hamiltonian is not time-reversal invariant, so that the state

$$|1s\,\overline{1s}\;2s\,\overline{2s}\,2p_-\overline{2p}_-\;2p_0'\overline{2p}_0'\,2p_+''\;\overline{2p}_+''|$$

has identical total energy.

The fact that the two positive-energy electrons are localized on the more diffuse $2p$ orbital has been more thoroughly studied. In Table VI the changes in such quantities as the total energy, and the $2p_+$ and $2p_0'$ orbital energies when one makes the fourth Slater $2p$ orbital more and more diffuse are shown. Clearly, limits are reached for these quantities, and these limits are identical with those reached in the case of a ^1D state for atomic oxygen. One can then assert that the intrinsic ellipsoidal Hartree-Fock state represents the system

$$(\mathrm{O}, {}^1D) + 2e^- .$$

There are no more closed-shell solutions.

The solution given in Table VII is no longer S^2 defined, but it is invariant by spin and space rotations about the quantization axis; in addition, the Fock Hamiltonian shows intrinsic symmetry properties in some respect intermediate between those of the Table IV and V Hamiltonians. The space of occupied orbitals splits into five-dimensional α and β subspaces, V_5^α and V_5^β, respectively.

The V_5^α subspace is invariant under the symmetry group of the ellipsoid. In V_5^β subspace, there is an intrinsic rotation axis. The α-spin electronic density is splitted from the β-spin density.

It is interesting to note that now just one electron has positive energy, suggesting an ionization in the form

$$(\mathrm{O}^{--}\ \mathrm{UHF\ axial}) \rightarrow \mathrm{O}^- + e^- .$$

The solution given in Table VIII is the only one with mixed spins. Although the mixing is relatively small, the change with respect to the last solution is significant as regards both the total energy and the spin-orbital energies (compare the $1s$, $2s$, and inner $2p$ orbitals in both solutions). The spin mixed solution is axially symmetric but although the Fock Hamiltonian has degenerate eigenvalues suggesting some intrinsic symmetry we have not been able to describe it in terms of geometrical symmetry operations. The suggested ionization is

$$(\mathrm{O}^{--}\ \mathrm{HF\ axial}) \rightarrow \mathrm{O} + 2e^- ,$$

but more calculations on O^{--}, O^-, and O would be needed.

The lowest energy solution, shown in Table IX, is an UHF one, no longer axially symmetric and with complex radial parts. Although quasidegenerate with the solution given in Table VIII, this is definitely different, as one is convinced on examination of the evolution of the orbital and total energies along the iterations. In the case under examination we indeed know that the diagonalized Fock Hamiltonian is unchanged by these 3×3 unitary transformations in $2p\alpha$ space, which mix the two spin orbitals ϕ_9 and ϕ_{10} and leave ϕ_8 unchanged; examination of the angular parts associated with each Slater-type orbital in ϕ_8, ϕ_9, and ϕ_{10} shows that these angular parts are common to all four radial parts, suggesting that some changes in the reference system could account for the observed degeneracy of ϕ_9 and ϕ_{10}. When one writes the conditions following the assumption that some (unitary) change in reference axis will reproduce the 3×3 transformations in $2p\alpha$ occupied space, one is confronted with a nontrivial matricial equation, and all that can be said up to now is that no proper rotation is convenient.

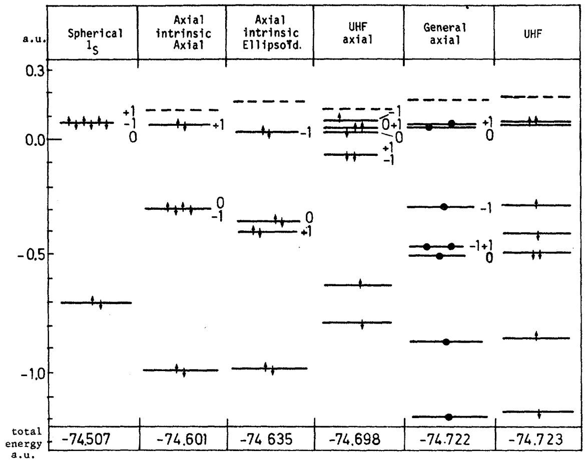

FIG. 1. One-electron energies diagram of six ground-state Hartree-Fock solutions for O^{--}.

We have summarized the results in Fig. 1. Ordinates are spin-orbital energies, $2p$ levels are labeled with their m value when possible, spin up and down are indicated by arrows and mixed spin by full point, $1s$ levels are not shown, and the dashed level is the first virtual level. From Fig. 1 one may then have an idea of the relative gaps.

Figure 1 shows that all closed-shell states have higher energies than open-shell ones, and that in each series the gap increases as total energy slows, indicating a greater stability of the lowest solutions. The last two Hartree-Fock solutions, quasidegenerate, are quasiequally stable. Our lowest Hartree-Fock solution is about 6 eV below the central-field one.

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[1] More precisely, if $\psi(LSM_LM_S)$ is some stationary state referred to an arbitrary z-quantization axis, the electronic density is an average over the energetically degenerate densities $\psi^*(LSM_L'M_S')\psi(LSM_L'M_S')$; that is, is proportional to

$$\sum_{M_S=-S}^{+S}\sum_{M_L=-L}^{+L}|\psi(LSM_LM_S)|^2 .$$

This is an invariant by any rotation or inversion, as $\psi^*(LSM_LM_S)=(-1)^{L-M_L}\times(-1)^{S-M_S}\psi(LS-M_L-M_S)$, and $(-1)^{L-M_L}$ is precisely the C-G coefficient to couple two L states to a resultant $L=0$ state, and similarly for S.

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[3] A variation $\delta\phi$, which is not orthogonal to ϕ, does not lead to variation of the energy $E(\phi)\equiv\langle H\rangle$.

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[6] Time-reversal transformation is not strictly speaking a symmetry transformation; however, if T is the associated operator, one has

$$T|\phi_1\cdots\phi_N|=|T\phi_1\cdots T\phi_N| .$$

We take phase conventions in angular momentum eigenfunctions such that

$$T|jm\rangle=(-1)^{j-m}|j-m\rangle .$$

In particular,

$$T\alpha=\beta,\quad T\beta=-\alpha ,$$

where α and β are spin $\frac{1}{2}$ and spin $-\frac{1}{2}$ eigenfunctions, respectively.

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