PHYSICAL REVIEW A VOLUME 19, NUMBER 2 FEBRUARY 1979

Pathological behavior of the open-shell restricted self-consistent-field equations

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(Received 7 March 1978)

The possible solutions of open-shell restricted self-consistent-field equations for a doublet are studied for Li and Na atoms, according to the values of the parameters implied in those equations. A similar behavior, characterized by the presence of several variational solutions is observed in both atoms. Some of these solutions can be assigned to excited configurations. Excitation energies are in good agreement with experimental data. Doublet stability for the solutions obtained has been studied, discussing the saddle-point character present in those solutions associated to excited configurations.

I. INTRODUCTION

The open-shell restricted self-consistent field theory (OSRSCF) has received much attention from the methodological point of view and multiple derivations for its pseudoeigenvalue equations are found in the literature.[1-5] The first serious approach to the problem is due to Roothaan[1] and although it has been successful in solving a large number of OSRSCF problems, it only applies to a limited series of electronic structures, treating them as an average of electronic states.

Every approach which attempts to reach the pseudoeigenvalue equations in a general form, and, therefore, valid for any electronic state, goes through the process of obtaining the appropriate couplings between shells by satisfying the Hermiticity of the undetermined Lagrange multipliers (ULM) matrix, via the following requirement

$$\langle \phi_k | F_i | \phi_i \rangle = 0\,, \tag{1}$$

where F_m is the Fock operator associated with the m shell and ϕ_m is an occupied orbital of that shell.

It has been shown[6] that equations derived after introducing condition (1) in the restricted Euler equations can lead to results which do not satisfy in general terms a stationary value for the energy as they depend on the values of the arbitrary parameters used by the above mentioned approaches.

This dependence suggests the possibility of finding practical solutions different from those of the ground state associated with the system chosen.

In the present work we have limited ourselves to Li and Na atoms both with doublet multiplicity and, therefore, with the simplest OSRSCF equations. Of all theories derived from condition (1), that of Huzinaga[4] shows a more general character; therefore, we shall be using his equations for the open-shell Hartree-Fock restricted model (OSRHF).

In Sec. II we study the possible solutions of OSRHF equations, as a function of the values taken by the parameters appearing in those equations, discussing the meaning of those solutions with an extremum character for the energy.

The presence of multiple solutions for the OSRHF equations (due to the sensitivity of these equations to the parameters introduced) requires a stability study of those solutions satisfying the extremum condition in order to define their nature from the variational point of view.

Finally, in Sec. III, a doublet stability analysis for the most significant solutions obtained in Sec. II is carried out, determining the sign of the second variation of the energy. A discussion of the saddle-point character found in those solutions associated with excited configurations is also included.

II. SOLUTIONS OF EQUATIONS OF OSRHF FOR ATOMIC DOUBLETS

For a two-shell electronic system, the OSRHF equations are

$$\begin{aligned} H^c\phi_i &= \epsilon_i\phi_i\,,\\ H^o\phi_k &= \epsilon_k\phi_k\,, \end{aligned} \tag{2}$$

the first applying to closed subshell orbitals, and the second to those of the open ones. H^c and H^o are the operators for the closed and open subshells, respectively. In Huzinaga's theory[4] those operators are defined in terms of the Fock operators (F^c, F^o) and the subshell projectors (P^c, P^o) as

$$\begin{aligned} H^c &= F^c - P^o(\mu_{co}F^c + (1-\mu_{co})F^o)\,,\\ H^o &= F^o - P^c(\mu_{oc}F^c + (1-\mu_{oc})F^o)\,, \end{aligned} \tag{3}$$

where μ_{co} and μ_{oc} are parameters taking any arbitrary values except the pair $\mu_{co}=1$ and $\mu_{oc}=0$ leading to Birss and Fraga equations.[2]

The iterative solution of Eq. (2) has been reached in two ways:

(i) The first way is by solving the single operator equation

$$H\phi = \epsilon\phi \tag{4}$$

with H defined as

$$H = H^c(1 - P^o) + H^o(1 - P^c)\ , \tag{5}$$

and where ϕ represents an orbital of the set defined by both subshells and the complementary subspace of the virtual orbitals.

Since the operator of Eq. (5) is not symmetrical, eigenvalues and eigenvectors of Eq. (4) have been reached by first obtaining the eigenvalues for the Hesenberg form associated to H and then the orthonormalized eigenvectors by using some recurrence expressions.[6]

(ii) The second way is by alternative diagonalization of the two symmetrical operators

$$\begin{aligned} R^c &= F^c - P^o[\mu_{co}F^c + (1 - \mu_{co})F^o] \\ &\quad - [\mu_{co}F^c + (1 - \mu_{co})F^o]P^o\ , \\ R^o &= F^o - P^c(\mu_{oc}F^c + (1 - \mu_{oc})F^o) \\ &\quad - (\mu_{oc}F^c + (1 - \mu_{oc})F^o)P^c\ , \end{aligned} \tag{6}$$

which satisfy Eq. (2) once the orthogonality between all orbitals is proved.

Orthogonality between orbitals of one subshell is assured since the rotation matrices, used to diagonalize the representation of the operators R^c and R^o, are orthogonal. This does not happen for orbitals of different subshells.

The expansion basis used in the present work is Gaussian type orbitals (GTO). For Li, a basis of the type $1s1s'\ 2s2s'\ 2s''\ 2s'''$ has been used, each of those functions being developed from six Gaussians. This basis has been chosen in order to approximate the Slater type orbitals (STO) basis optimized by Clementi,[10] for the Li ground state, with identical exponents. The energy found with the STO basis for Li ground state is −7.432 727 a.u.

The majority of the calculations carried out for the Na atom use a minimal basis set with each orbital constructed as a contraction of four Gaussian functions.

Figure 1 shows the results obtained with level *i* for Li using a wide range of μ_{co} and μ_{oc} values. It shows two zones (I, II) the first, characterized by the convergence to a single energy value (− 7.430 679 a.u.), is the variational solution of the ground state and satisfies the nullity of Eq. (1). Zone II is characterized by a random behavior in the SCF process, with no convergence to any value of the energy being observed in the cases studied. Line (a) of Fig. 1, passing through the point $\mu_{co} = 1$ and parallel to the axis μ_{oc}, presents a series of convergent solutions (which we define as a particular family dependent on μ_{oc}) including the solution of Birss and Fraga's theory[2] ($\mu_{oc} = 0$, $\mu_{co} = 1$) previously discussed.[6,7]

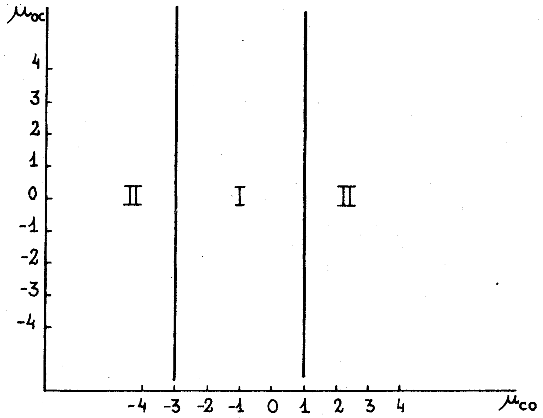

FIG. 1. Li atom; level *i* result. Convergence zones to a definite energy value.

None of the solutions of the family that corresponds to line (a) satisfy the nullity of (1), and consequently they must be considered as nonvariational SCF solutions.

The calculations carried out for level *i* are an extension of a previous analysis[6] and add no characteristics to those already found. Calculation for every solution obtained have been made with different trial orbitals, and only those of family (a) are sensitive to the selection of the initial functions. Without a deeper analysis this finding could lead to the mistaken conclusion that every variational solution corresponds to a minimum value of the energy.

Figures 2 and 3 show the results obtained by diagonalizing alternatively the operators of level *ii* [Eq. (6)]. The zones in which Figs. 2 and 3 have been divided represent points in the plane μ_{oc}, μ_{co}, leading to the same solution. Outside those zones, convergence in the iterative process was not observed. In both figures, zone I corresponds to the ground-state solution, with an energy of −7.430 679 and −160.702 006 a.u. for the Li and Na atoms, respectively. The orbitals associated with each of those solutions are orthonormal and the integral of Eq. (1) is zero in both cases, which indicates, that they are extrema values of the energy.

Zones II and III in Fig. 2 correspond to solutions contradicting the antisymmetry principle, yielding three spin orbitals with the same spatial part (one of them is associated to the open-subshell operator R^o). This is a surprising result since one would not expect a definition of the couplings be-

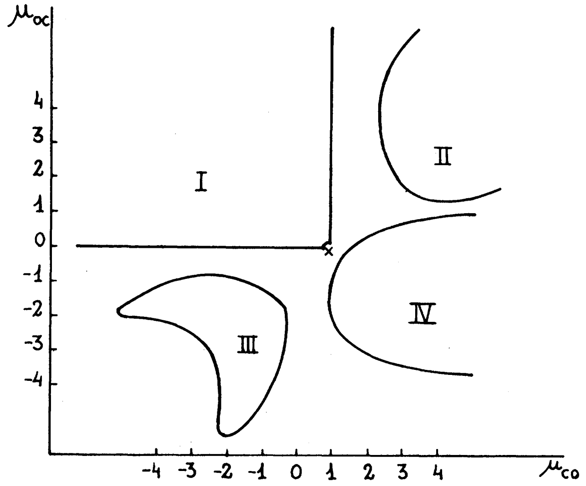

FIG. 2. Li atom; level *ii* results. Convergence zones to a definite energy value. Boundaries of zones II, III, and IV are approximate since no exact borderline exists between convergence zones and those with no convergence. Point × correspond to Birss and Fraga.

tween shells (even when imperfect) which only forces the ULM Hermiticity, to provoke the severance of a constraint as strong as the antisymmetry condition.[8] It is obvious that this type of solution, as well as those associated with nonorthogonal orbitals, must be discarded as it does not satisfy the requisites established for obtaining OSRSCF equations.

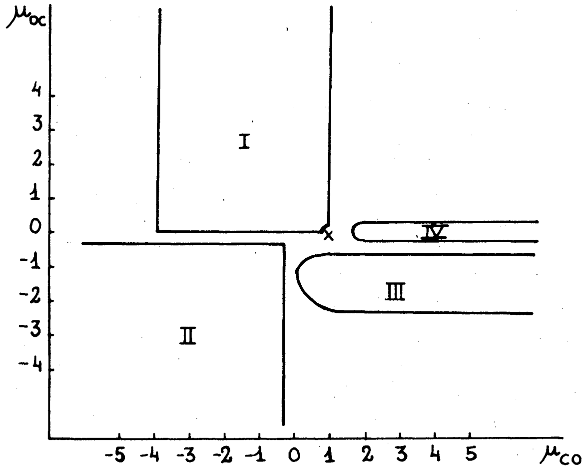

FIG. 3. Na atom; level *ii* results. Convergence zones to a definite value of the energy. Boundaries of zones II, III, and IV are approximate since no exact borderline exists between convergence and nonconvergence zones. Point × corresponds to Birss and Fraga's theory, with energy −160.567 277 a.u.

TABLE I. Energy levels in a.u. for the three solutions encountered for the Li atom. The second eigenvalue corresponds to the open-shell occupied orbital.

Solution	ϵ_1	ϵ_2
Ground state	−2.4770	−0.1963
Birss-Fraga	−2.4538	−0.2136
Excited	−0.2803	−3.6379

Zone IV in Fig. 2 merits a more detailed study. The energy obtained is −5.340 913 a.u. and the orbitals associated with this solution are orthonormal and satisfy the nullity of Eq. (1). This solution satisfies all requirements demanded of a stationary value.

Analysis of the orbitals shows that the one of the closed subshells is of the $2s$ type while the singly occupied one is $1s$. Table I presents the eigenvalues, in both subshells, for the fundamental, Birss and Fraga, and zone-IV solutions. From those eigenvalues and from the form of the orbitals it is inferred that $1s2s^2$ is the configuration associated to the solution with energy −5.340 913. This solution corresponds to an excited state generated by the promotion of an electron from the inner shell to orbital $2s$, with an excitation energy of 56.87 eV.

Experimental data obtained by collisional excitation[9] assign for the optically forbidden transition ($2s \leftarrow 1s$) for Li, an excitation energy of 56.31 eV, in excellent agreement with present results. The wave functions associated with ground and excited states, although nonorthogonal, show a scalar product of 0.0013.

Region II, in Fig. 3, corresponding to the Na atom, represents a solution which contradicts Pauli's principle. This is also true for the Li atom, as mentioned above.

Regions III and IV in Fig. 3 represent two solutions that satisfy the extremum condition for the energy, with the orthogonality condition also satisfied for the orbitals of each solution. Again, the solution associated to region IV can be classified as an excited state with electronic configuration $1s^22s^22p^53s^2$ and energy −159.505 898 a.u. In this case, excitation energy from the ground state is 32.54 eV.

Analysis of orbitals and eigenvalues of the region-III solution indicates an excited state with configuration $1s2s^22p^63s^2$, energy −120.839 970 a.u., and excitation energy associated to the transition $3s \leftarrow 1s$, 1084.64 eV.

From the previous results, and those obtained for Li, a variational solution associated to another excited state $1s^22s2p^63s^2$ for Na should be expected.

TABLE II. Energy levels in a.u. for the three solutions encountered for the Na atom. The last eigenvalue corresponds to the open-shell occupied orbital. Upper indices *t* and *d* indicate triply and doubly degenerate eigenvalues, respectively.

Solution	ϵ_1	ϵ_2	ϵ_3	ϵ_4	ϵ_5
Ground state	−40.4599	−2.7848	-1.5172^t	−0.1870	⋯
Excited ($2p$)	−41.2187	−3.2998	-2.0621^d	−0.2428	−2.2303
Excited ($1s$)	−3.5819	-2.3609^t	−0.2491	−45.1589	⋯

That solution, however, has not been found.

Since the numerical results obtained in the calculations with the minimal basis cannot be used for quantitative purposes, the three most significant solutions found for Na (ground and the two excited states) have been computed again with a double-zeta-type basis ($1s1s'$ $2s2s'$ $2p2p'$ $3s3s'$) and every orbital constructed by contraction of six Guassians (see Table II). This basis is of similar quality to the STO one, optimized by Clementi[10] for the Na ground state with the same values for the exponents. The energy found with the STO basis for Na ground state is −160.849 730 a.u.

Energies found for open-shell configurations $3s$, $2p^5$, and $1s$, are −161.809 085, −160.665 356, and −122.416 863 a.u., respectively. The transition energies found are 31.13 eV ($3s \leftarrow 2p$) and 1074.52 eV ($3s \leftarrow 1s$). The optically active transition $3s \leftarrow 2p$, has been experimentally observed using photoabsorption techniques[11] and also by induced collisional excitation.[9]

The energy associated to this transition is 30.93 eV,[12] which agrees well with present calculations.

Unfortunately, we do not have experimental data for the optically forbidden transition ($3s \leftarrow 1s$). Nevertheless, the result obtained here is quite reasonable if one compares it to the monoelectronic energy of level $1s$ for the ground state, and if one assumes Koopman's theorem as a valid approximation.

Orthogonality between variational solutions obtained for Na is satisfactory since the scalar product between the wave functions associated to configurations $1s^2 2s^2 2p^6 3s$ and $1s 2s^2 2p^6 2s^2$ is 0.0038. The scalar product between those wave functions and that of configuration $1s^2 2s^2 2p^5 3s^2$ is zero for symmetry reasons.

III. STABILITY ANALYSIS FOR SCF SOLUTIONS

Conditions for doublet stability in OSRHF equations have been formulated by Paldus and Cizĕk,[13] where they were applied in their study of linear polyens instability, following the semiempirical formalism of PPP.[14] Yamaguchi and Fueno[15] have studied both nondoublet and spin-flipping instabilities in free-radical dissociation processes.

In this section we present the results of a doublet stability study carried out over the SCF solutions presented in Sec. II. Nondoublet instabilities are not considered here since we are exclusively interested in the stability of our solutions within the set of possible solutions restricted by spin and spatial part.

The stability criterion followed here is based on the sign of the second variation for the energy, implying calculation of the eigenvalues of the matrix:

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix}, \tag{7}$$

where A is the matrix grouping interactions between all possible monoexcitations compatible with the OSRHF model and B is the matrix containing interactions between the configuration under study and all possible biexcitations, also compatible with the model.

To deduce the matrix elements for a doublet term in the restricted Hartree-Fock (RHF) approximation is a laborious process and it is included

TABLE III. Li atom. Eigenvalues λ and λ' for matrices $A+B$ and $A-B$, respectively.

Solution	λ_1	λ_2	λ_3	λ_4	λ_1'	λ_2'	λ_3'	λ_4'
Ground state	0.123 05	0.292 22	1.614 88	2.199 45	0.123 07	0.292 30	1.616 29	2.195 83
Excited	−2.035 68	0.396 38	0.711 49	2.742 15	−2.018 46	0.368 49	0.604 52	2.628 8
Birss-Fraga	0.134 99	0.304 65	1.635 08	2.152 48	0.134 72	0.303 85	1.633 33	2.150 95

in the paper by Paldus and Čizek.[13,16] With real orbitals, as in the present case, matrix (7) can be written in real form as a block diagonal matrix

$$\begin{pmatrix} A+B & 0 \\ 0 & A-B \end{pmatrix} \qquad (8)$$

such that submatrices $A+B$ and $A-B$ correspond to variations in real and imaginary spaces, respectively.[17]

For Li, stability of solutions for the ground and excited states, as well as that for the theory of Birss and Fraga, have been studied. Table III show the four lowest eigenvalues associated to submatrices $A+B$ and $A-B$ from (8).

For the ground state, all eigenvalues are positive, thus indicating that it is a minimum (whether it is local or absolute is not in the scope of this analysis and therefore every time a minimum appears its local character will be assumed).

The smallest eigenvalue associated with the excited state is negative, which implies the presence of a saddle point. Obtaining a single negative solution for matrix $A+B$ indicates the existence of a stable solution with real orbitals, below the one studied and corresponding in this case to the fundamental state previously found.

Eigenvalues associated to Birss and Fraga type of solution are all positive, implying initially that such a solution is a relative minimum. However, the sign of the second variation for the energy as a stability criterion is conditioned to the nullity of the first variation and, as shown previously, this is not true for solutions associated to line (a) of Fig. 1.

Figure 4 presents the energy associated with the solutions of line (a) as a function of μ_{co}. It shows that the curve tends to a minimum, associated with the ground state, when $|\mu_{co}|$ increases. It also shows the Birss and Fraga solution does not correspond to an extremum for μ_{co}. Here is an example of how studying the sign of the second variation for the energy can lead to wrong conclusions about a solution's stability unless it is followed by an analysis of the solution's extremum character.

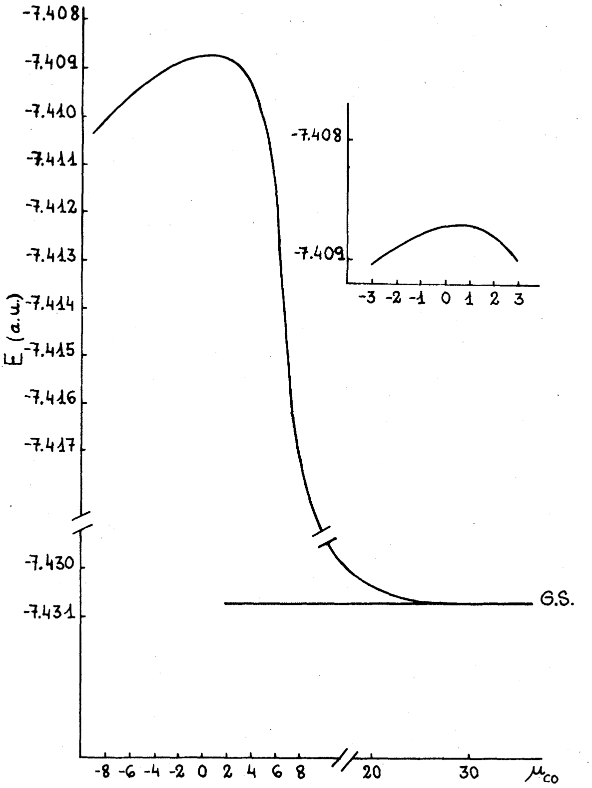

FIG. 4. Representation of line (a) (Fig. 1) as an energy function vs μ_{co}. G.S. is the energy obtained for the ground state.

Table IV shows the lowest eigenvalues for submatrices $A+B$ and $A-B$ of (8) associated with ground, first-excited ($3s \leftarrow 2p$), and second-excited ($3s \leftarrow 1s$) solutions for Na. Eigenvalues for the ground state are all positive, indicating that it is a minimum.

If matrices $A+B$ and $A-B$ of (8) present two or more negative or zero eigenvalues, the solution is a multiple unstable saddle point. Negative eigenvalues above the lowest one, are connected to one or more minima through unstable points in the scalar space associated with the Hamiltonian. This is the case of the two excited solutions obtained for Na.

TABLE IV. Na atom. Eigenvalues λ and λ' for matrices $A+B$ and $A-B$, respectively. Upper indices t and d indicate triply and doubly degenerate solutions, respectively.

Solution	λ_1	λ_2	λ_3	λ_4	λ_1'	λ_2'	λ_3'	λ_4'
Ground state	0.297 33	0.92541	$2.266\,77^t$	$2.316\,16^t$	0.29740	0.92388	2.2174^t	$2.314\,81^t$
Excited ($3s \leftarrow 2p$)	−0.836 34	0.0000^d	0.619 73	1.391 24	−0.83625	0.0000^d	0.68678	1.399 13
Excited ($3s \leftarrow 1s$)	−39.596 10	-38.7800^t	−37.406 20	0.590 42	−39.5952	-38.7820^t	−37.3922	0.467 68

The first excited state has a negative eigenvalue, related to the ground state, and with an absolute value similar to that of the energy implied in the $3s \leftarrow 2p$ excitation. The second eigenvalue is zero and it is doubly degenerate. Its existence can be explained considering that the excited state is not the result of an average (as it would have been using Roothaan's theory) but it is generated by the promotion of an electron from a $2p$ orbital; therefore, two degenerate solutions must always exist with the one studied.

Three negative eigenvalues are found for the second excited state indicating that it is a saddle point. From their moduli it can be inferred that they are related to the ground state obtained here. The lowest eigenvalue is directly related to the fundamental state, while the second is triply degenerate and related to the ground state through the first excited state which has the same degeneracy as the eigenvalue.

The third eigenvalue (nondegenerate), suggests the possible existence of an unstable solution, associated to the $3s \leftarrow 2s$ transition, which, as pointed out before, has not been found here.

We are currently extending the treatment presented here to study possible excited solutions in molecules with doublet mutliplicity and we shall be reporting the results in a future paper.

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$$F^c = h + \sum_j (2J_j - K_j) + \sum_k (J_k - \tfrac{1}{2}K_k),$$

$$F^o = \frac{1}{2}\left(h + \sum_j (2J_j - K_j) + \sum_k (J_k - K_k)\right).$$

The presence of solutions contradicting Pauli's principle, can be explained as a consequence of using assumptions valid only in convergence when giving explicit form to the ULM present in Euler's equations:

$$F_c\,\phi_i = \epsilon_i\,\phi_i + \sum_k \epsilon_{ik}\phi_k,$$

$$F^o\,\phi_k = \epsilon_k\phi_k + \sum_i \epsilon_{ki}\phi_i.$$

For a more detailed discussion about this point, see Ref. 6.

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