Stability of the closed-shell atomic configurations with respect to variations in nuclear charge

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In this paper we systematically investigate the stability of the restricted Hartree-Fock (RHF) solutions for all closed-shell atoms and ions up to xenon-like systems by means of a symmetry-adapted Thouless stability matrix. We express the RHF solution and the lowest eigenvalue of the stability matrix in the form of a series in $1/Z$; Z is the nuclear charge. Using Padé and Weniger sequence transformations, we first determine the onset of the pure singlet instability, i.e., the instability preserving all the symmetries of the underlying Hamiltonian, and identify it with the critical charge Z_c, i.e., the smallest charge supporting a bound-state RHF solution. This thus finally gives a physical meaning to the pure singlet instability. Consequently, we find that no basis-set-independent RHF solution for any doubly charged anion exists. Second, we determine the onset of instabilities associated with the breaking one of the symmetries of the Hamiltonian and give a simple qualitative criterion for their appearance. In particular, we find that once the shells are no longer filled according to the Aufbau principle for hydrogenic energy levels, cations are generally unstable with respect to monoexcitations violating the spherical symmetry.

I. INTRODUCTION

The independent particle model (IPM) [1] is a starting point of the vast majority of *ab initio* calculations of the atomic and molecular electronic structure. Depending on whether the IPM wave function does or does not satisfy all the symmetries of the underlying Hamiltonian, one generally distinguishes a restricted Hartree-Fock (RHF) or an unrestricted HF (UHF) model. RHF equations yield a symmetry-adapted solution (SAS). UHF equations lead generally to a broken-symmetry solution (BSS), but, of course, the SAS solves the UHF equations as well.

The question of whether the SAS lies above or below a BSS can can be investigated by calculating the lowest eigenvalue of the stability matrix, first introduced by Thouless [2]. The advantage of this approach is that the stability of the found SAS can be investigated without actual calculation of a BSS: If the eigenvalue is negative (positive), the SAS is unstable (stable). The stability matrix is constructed using monoexcitations from the SAS. These monoexcitations can be symmetry adapted according to the symmetries of the underlying Hamiltonian, and consequently the stability matrix factorizes into a block-diagonal form. This was noted for the first time by Čížek and Paldus [3,4], who considered spin-preserving (singlet) and spin-violating (triplet or nonsinglet) types of instabilities. The physical meaning of the instabilities has been assigned as follows: besides a SAS there is a BSS of lower energy that violates the spin symmetry in the triplet case and the spatial symmetry of the fixed nuclear framework in the singlet case; cf. [5]. The difficult, and still not fully resolved, question is whether the HF symmetry breaking is real or artifactual, i.e., whether symmetry breaking does or does not survive when electronic correlation is taken into account; cf. [5,6]. The symmetry adaptation of the stability matrix was later extended to include also discrete symmetries for a generic molecular Hamiltonian in [7–10].

In the case of an atomic Hamiltonian, there are in general five operators commuting with the Hamiltonian, namely, $\hat{S}^2$, $\hat{S}_z$, $\hat{L}^2$, $\hat{L}_z$, $\hat{\Pi}$, where $\hat{\mathbf{S}}$, $\hat{\mathbf{L}}$, and $\hat{\Pi}$ stand for the total spin, total angular momentum, and parity operators, respectively. The monoexcitations generally conserve S_z and L_z [11], but not $S(S+1)$, $L(L+1)$, and Π. When using symmetry-adapted monoexcitations, one of the blocks of the stability matrix preserves all the symmetries of the Hamiltonian. This block will be termed as a *pure singlet* stability matrix, to distinguish it from the above-mentioned molecular case, where the singlet stability matrix consists of a mixture of a pure stability matrix and a stability matrix violating other than spin symmetry (usually spatial).

The purpose of this paper is twofold. First we would like to elucidate the physical meaning of pure singlet instability, which has been still generally unclear. Second, we would like to systematically search for onsets of instabilities of RHF solutions for closed-shell atomic systems [12] associated with the breaking one of the symmetries of the Hamiltonian. In the forthcoming papers we would like to explore consequences of this phenomenon for calculation of the correlation energy.

To achieve these goals we first show that a SAS can be obtained via a perturbative expansion of the RHF equations in the form of the series in $1/Z$ [13]. We then determine radii of convergence of the series, which correspond to so-called critical charges Z_c. For $Z < Z_c$ the electronic correlation is so strong that no bound-state SA HF solution for the given atom exists. Next, we construct an expansion in the powers of $1/Z$ for the lowest eigenvalues $\lambda_{S,L,\Pi}(Z)$ of the blocks

of the symmetry-adapted stability matrix. We need to sum this expansion outside its radius of convergence; therefore we use Padé and Weniger sequence transformations, see, e.g., [14,15], to search for the onset of instabilities. That is, we search for values of the charges $Z_i(S, L, \Pi)$ such that $\lambda_{S,L,\Pi}(Z = Z_i(S, L, \Pi)) = 0$. At this point, the stable SAS becomes unstable or vice versa. The main advantage of this perturbative approach is that we can obtain information about the behavior of the SAS in the region of strong electron correlation where the usual self-consistent (SC) method fails. Also, the onset of instabilities is obtained much more efficiently within the perturbative approach developed here than via the SC method. We present numerical evidence that $Z_i(0, 0) = Z_c$ [16], i.e., that the pure singlet instability corresponds to the case when no bound-state SA HF solution exists. This gives a physical meaning to the pure singlet instability.

While there are works focusing on RHF instabilities for atoms, see for example [17], no systematic study of the entire Mendeleev periodic table (up to Xe) has been carried out. Also while there have been several suggestions for alternative numerical algorithms to the SC procedure, see, e.g., [18], some of them even with a mathematical level of rigor [19,20], they are limited to specific cases and none of them allows one to draw a clear demarcation line between the cases where RHF does not exist at all and where it does exist, but is difficult to obtain.

The paper is organized as follows. In Sec. II we recapitulate briefly RHF equations and criteria for the stability of their solutions. In Sec. III we present and discuss our results. Our findings are summarized in Sec. IV.

II. THEORY

A. Restricted Hartree-Fock equations

The RHF model is a well-known approximation; see, e.g., [21]. Therefore we restrict ourselves here to the bare minimum needed for a coherent presentation.

We put successively $2N$ electrons into ν shells labeled by a; in a given shell a there are $2(2l_a + 1)$ states of the form $\phi_{n_a, l_a}(r) Y_{l_a, m_a}(\mathbf{n}) |s_a\rangle$, where $Y_{l,m}(\mathbf{n})$ are spherical harmonics and magnetic quantum number m_a runs from $-l_a$ to l_a by 1 and $|s_a\rangle = |\frac{1}{2}, \pm\frac{1}{2}\rangle$ are the spin states. This is commonly referred to as the central field or shell model; the spin and angular parts of the one-electron functions are held fixed; the radial parts are optimized.

Using by now standard methods (see, e.g., [21]) one easily derives that the nonrelativistic RHF equations for a closed-shell atom with $2N$ occupied spin orbitals read (we rescaled the electronic coordinates $\mathbf{r}^{(i)} \rightarrow \mathbf{r}^{(i)}/Z$)

$$\hat{f}_a|a\rangle = \epsilon_a|a\rangle, \quad \hat{f}_a|a\rangle_1 = \hat{h}_0^{l_a}|a\rangle_1$$
$$+ \frac{1}{Z} \sum_{b=1}^{\nu} \frac{2l_b + 1}{\langle b|b \rangle} \langle b|_2 (2\hat{v}_c|a\rangle_1|b\rangle_2 - \hat{v}_e|b\rangle_1|a\rangle_2), \quad (1)$$

where the one-electron energies ϵ_a are related to the total energy via the relation

$$\frac{E}{Z^2} = \sum_{a=1}^{\nu} (2l_a + 1)\left(\epsilon_a + \frac{\langle a|\hat{h}_0^{l_a}|a\rangle}{\langle a|a \rangle}\right). \quad (2)$$

Here, $|a\rangle$ are the radial orbitals in the abstract notation; their projections onto the coordinate basis are the radial functions $\langle r|a\rangle = \phi_{n_a, l_a}(r)$. Furthermore, $\hat{h}_0^l$ is the radial part of the hydrogenic Hamiltonian,

$$\hat{h}_0^l = \frac{1}{2}\left[\hat{p}_r^2 + \frac{l(l+1)}{r^2}\right] - \frac{1}{r}, \quad \hat{p}_r = -i\left(\frac{\partial}{\partial r} + \frac{1}{r}\right), \quad (3)$$

and the radial operators of the Coulomb and exchange interaction read

$$\hat{v}_c = r_>^{-1}, \quad \hat{v}_e = \sum_{l=|l_a-l_b|}^{l_a+l_b} \frac{r_<^l}{r_>^{l+1}} \frac{(l_a, 0, l_b, 0|l, 0)^2}{2l+1}, \quad (4)$$

where $r_< = r_1, r_> = r_2$ if $r_1 < r_2$ and $r_< = r_2, r_> = r_1$ if $r_1 > r_2$; $(l_1, i, l_2, m - i|l, m)$ are Clebsch-Gordan coefficients.

Equations (1) are most easily solved by expanding the sought radial functions into the scaled Sturmian basis set, see, e.g., [22–24],

$$\phi_{n_a, l_a}(r) = \sum_{j=l_a+1}^{l_a+N} \frac{c_{j,a}}{n_a} R_{j,l_a}(r/n_a). \quad (5)$$

The Sturmian functions are solutions of the eigenvalue problem

$$\left\{\frac{r}{2}\left[\hat{p}_r^2 + \frac{l(l+1)}{r^2}\right] + \frac{r}{2}\right\} R_{n,l}(r) = n R_{n,l}(r), \quad (6)$$

where n is natural number. They are related to hydrogenic functions $R_{n,l}^h$ by the simple relation $R_{n,l}^h(r) = \frac{1}{n^2} R_{n,l}(r/n)$.

Projecting the RHF equations (1) onto the Sturmian basis set we transform these equations into algebraic RHF equations. These equations have the form of a pseudoeigenvalue problem; the eigenstates comprise the coefficients $c_{j,a}$ and the eigenvalues are the one-particle energies ϵ_a. The pertinent matrix elements are calculated using a numerically stable method developed in [23]. The algebraic RHF equations are usually solved by the SC method. Alternatively, one can solve algebraic RHF equations by expanding the energy ϵ_a and the coefficients $c_{i,a}$ into a perturbation series in the inverse powers of the nuclear charge Z,

$$\epsilon_a = \sum_{r=0}^{\infty} z^r \epsilon_a^{(r)}, \quad c_{i,a} = \sum_{r=0}^{\infty} z^r c_{i,a}^{(r)}, \quad z = 1/Z, \quad (7)$$

where

$$\epsilon_a^{(0)} = -\frac{1}{2n_a^2}, \quad c_{i,a}^{(0)} = \frac{\delta_{i,n_a}}{\sqrt{n_a}}. \quad (8)$$

Note that the generation of the terms of the perturbation series is enormously simplified by imposing the normalization condition $\langle b|b \rangle = 1$.

B. Symmetry-adapted stability matrix

The HF equations arise from the requirement that the first variation of energy in the space of monoexcitations vanishes. However, this requirement does not ensure that the found solution is indeed a local minimum, for $\delta^{(1)}E = 0$ leads to any extremal point, i.e., also to (local) maxima and saddle points. Therefore, only if the second variation of energy is positive, $\delta^{(2)}E > 0$, the found solution, corresponding indeed to a local

minimum, is said to be stable. Thus we construct the matrix Λ of the second variations in the space of monoexcitations; see Eqs. (9) and (11) below. As is well known, the sufficient condition for an extreme to be a local minimum is that the lowest eigenvalue of the corresponding Hessian matrix is positive. Therefore the sign of the lowest eigenvalue of the matrix Λ, see Eq. (13) below, determines the (in)stability of the found RHF solution.

For closed-shell systems the spin-adapted stability matrices read for a real basis [3,4]

$$
\begin{aligned}
\Lambda_{a,b}^{S} &= \delta_{o_a,o_b}[f_{o^a,o^b} - \delta_{o^a,o^b}\epsilon_a] \\
&+ \frac{1}{Z}\big\{2(r_{12}^{-1})_{o^a o^b, o_a o_b}[1 + (-1)^S] \\
&- (r_{12}^{-1})_{o^a o^b, o_b o_a} - (r_{12}^{-1})_{o^a o_b, o^b o_a}\big\}.
\end{aligned}
\tag{9}
$$

The stability matrix is expressed here in the basis of monoexcitations labeled by a and b. Each monoexcitation a is determined by the occupied and virtual *orbitals* labeled by o_a and o^a, respectively. These orbitals are eigenstates of the Fock operator. Finally, $S = 0$ and $S = 1$ correspond to spin-conserving (singlet) and spin-violating (triplet) stability matrices, respectively. The Fock matrix in Eq. (9) is defined as

$$
f_{o^a,o^b} = (\hat{h}_0)_{o^a,o^b} + \frac{1}{Z}\sum_{o_c}\big[2(r_{12}^{-1})_{o^a o_c, o^b o_c} - (r_{12}^{-1})_{o^a o_c, o_c o^b}\big],
\tag{10}
$$

where the summation in the last equation runs through all occupied orbitals, $\hat{h}_0$ is a one-electron Hamiltonian for the kinetic energy of the electron and its potential energy in the Coulomb field of the nucleus, $\hat{h}_0 = -\frac{\nabla^2}{2} - \frac{1}{r}$, and r_{12}^{-1} is the inverse distance between two electrons.

In the case of atoms the occupied and virtual orbitals in (9), o_a and o^b, are uniquely defined by the triples of quantum numbers (n_a, l_a, m_a) and (n^a, l^a, m_a), respectively. The matrix (9) can thus be further factorized according to the total angular momentum L and parity Π of the monoexcitations,

$$
\begin{aligned}
\Lambda_{a,b}^{S,L,\Pi} &= \sum_{m_a=-l_a}^{l_a}\sum_{m_b=-l_b}^{l_b}(l^a, m_a, l_a, -m_a|L, 0) \\
&\times (l^b, m_b, l_b, -m_b|L, 0)(-1)^{m_a+m_b}\Lambda_{a,b}^{S},
\end{aligned}
\tag{11}
$$

where the parity of the monoexcitation is defined as

$$
(-1)^{\Pi} = (-1)^{l^a+l_a} = (-1)^{l^b+l_b}.
\tag{12}
$$

Note that with this symmetry adaptation, each monoexcitation a is characterized by quantum numbers (n_a, l_a, n^a, l^a), where n_a, l_a and n^a, l^a are principal, orbital quantum numbers of the occupied and virtual orbitals, respectively.

To investigate the stability of the RHF solution we solve the eigenvalue problem (we suppress the superscripts S, L, Π),

$$
\hat{\Lambda}|\lambda\rangle = \lambda|\lambda\rangle.
\tag{13}
$$

According to the sign of the *lowest* eigenvalue λ, the RHF solution is stable (if $\lambda > 0$) or unstable (if $\lambda < 0$). The corresponding eigenvector gives the direction of the steepest descent ($\lambda < 0$) or the slowest ascent ($\lambda > 0$) on the mean energy hypersurface [3,4].

We found that for obtaining global insight about stability of the given electron configuration in the field of the nucleus with respect to variation of the nuclear charge, it is advantageous to search again for the solution of Eq. (13) in the form of the series in inverse powers of nuclear charge Z:

$$
|\lambda\rangle = \sum_{r=0}^{\infty}|\lambda_r\rangle z^r, \quad \lambda = \sum_{r=0}^{\infty}\lambda_r z^r, \quad z = 1/Z,
\tag{14}
$$

where the zeroth-order solution reads, cf. Eqs. (9) and (10) in the limit of $Z \to \infty$,

$$
\lambda_0 = \frac{1}{2}\left(\frac{1}{n_{\text{HO}}^2} - \frac{1}{n_{\text{LU}}^2}\right), \quad \langle r|\lambda_0\rangle = \frac{1}{n_{\text{LU}}^2}R_{n_{\text{LU}},l^{\text{HO}}}(r/n_{\text{LU}}),
\tag{15}
$$

where the radial functions R are defined by Eq. (6). Further, n_{HO} denotes the principal quantum number of the occupied orbital with the highest hydrogenic energy and n_{LU} and l^{HO} denote the principal and orbital quantum numbers of the virtual orbital with the lowest hydrogenic energy, respectively. For example, in the case of neon-like systems, there are two occupied orbitals with the highest hydrogenic energy ($2s$ and $2p$) and three virtual orbitals with the lowest hydrogenic energy ($3s$, $3p$, and $3d$). Thus, in general, one has to employ the degenerate perturbation method; see [25].

The physical reasoning behind the choice of the zeroth-order solution is the following: As the nuclear charge Z increases, the role of the electron-electron interaction diminishes; cf. Eq. (1). In the limit $Z \to \infty$, the one-particle energies ϵ_a become that of the hydrogen, $\epsilon_a = -(2n_a)^{-2}$. In this limit, the lowest eigenvalue of the stability matrix is then simply the difference between the lowest unoccupied hydrogenic orbital and the highest occupied hydrogenic orbital [26]. It turns out, see next section, that the stability of the given electronic configuration with respect to variation of the nuclear charge can be classified according to the sign of λ_0 (see Fig. 1 for illustration):

(i) $n_{\text{LU}} > n_{\text{HO}}$. This is the only possible case when all hydrogenic shells with different orbital quantum numbers l for a given n are occupied. The only such systems are helium-like and neon-like; otherwise we have to consider also the other possibilities listed below.

(ii) $n_{\text{LU}} = n_{\text{HO}}$. This is the most complex case and appears whenever not all of the shells with different l for a given n are occupied; cf. [27]. The first such case appears for beryllium-like atoms, where the $2s$ shell is occupied, but not the $2p$ shell; the pertinent hydrogenic monoexcitation is $(2, 0; 2, 1)$.

(iii) $n_{\text{LU}} < n_{\text{HO}}$. This appears whenever the atomic shells are not filled in accordance with the Aufbau principle for hydrogenic levels. The first such case appears for calcium-like atoms where the $4s$ orbital is filled earlier than the $3d$ orbital; the pertinent $L = 2$, $\Pi = 0$ hydrogenic monoexcitation is $(4, 0; 3, 2)$ (see Fig. 1). The next case is a strontium-like system where the $5s$ orbital is filled earlier than the $4d$ and $4f$ orbitals; the pertinent $L = 2$, $\Pi = 0$ and $L = 3$, $\Pi = 1$ hydrogenic monoexcitations are $(5, 0; 4, 2)$ and $(5, 0; 4, 3)$, respectively.

The calculation of the higher-order terms of the series (7) and (14) is relatively straightforward, albeit somewhat laborious; for details see [25].
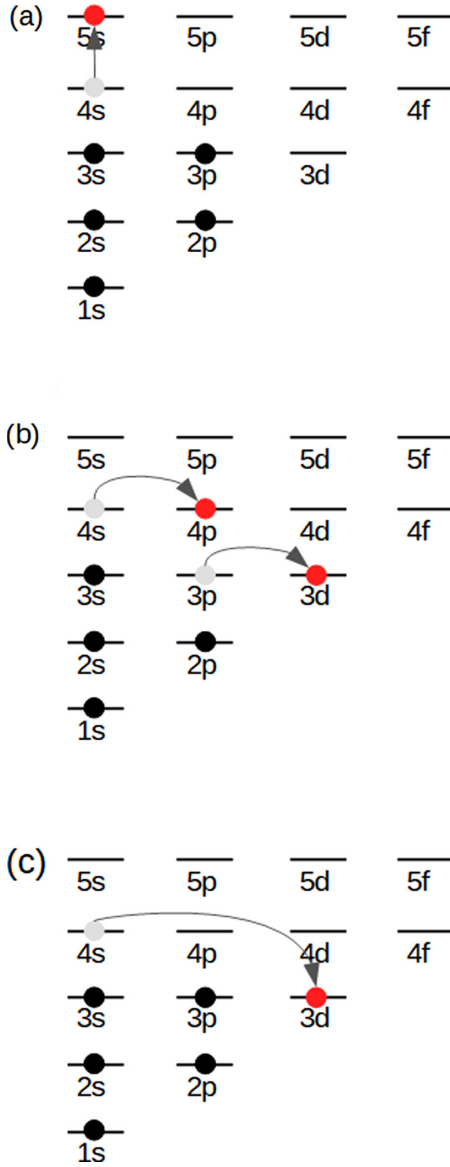
FIG. 1. Illustration of the three types of monoexcitations, see Sec. II B, for Ca-like atoms. The black dots represent occupied orbitals that do not participate in the monoexcitation. The gray dots mark the shell from which we excite and the red dots mark the virtual orbital to which we excite. Case (a): $L = 0$. The lowest unoccupied (LU) hydrogenic orbital lies above the highest occupied (HO) hydrogenic orbital, i.e., $n_{LU} > n_{HO}$; the shown monoexcitation is $(4, 0; 5, 0)$. Hence $\lambda_0 > 0$. Case (b): $L = 1$, $\Pi = 1$. The LU hydrogenic orbital has the same energy as the HO hydrogenic orbital, i.e., $n_{LU} = n_{HO}$; the shown monoexcitations are $(4, 0; 4, 1)$ and $(3, 1; 3, 2)$. Hence $\lambda_0 = 0$. Case (c): $L = 2$, $\Pi = 0$. The LU hydrogenic orbital lies below the HO hydrogenic orbital, i.e., $n_{LU} < n_{HO}$; the shown monoexcitation is $(4, 0; 3, 2)$. Hence $\lambda_0 < 0$.

III. RESULTS AND DISCUSSION

Standard analytic HF calculations [28] are, in practice, plagued by the limitations of a finite basis size. In calculations such as those in this study the basis size proved to play a crucial role and very large bases had to be used to eliminate their effect on the results. Specifically, we observed strong

TABLE I. Values of the nuclear charge $Z_i(S, L, \Pi)$ for which the first zero root appears among the eigenvalues of the singlet ($S = 0, L = 0, \Pi = 0$) and spin triplet ($S = 1, L = 0, \Pi = 0$) stability matrices. The results were obtained using Weniger (w) or Padé (p). Z_c is the radius of convergence of the perturbative series for total energy.

	Z_c	$Z_i(0, 0)$	$Z_i(1, 0)$
He-like	0.82	$0.8(2)^p$	1.06^p
Be-like	2.87(3)	2.84^w	3.04^w
Ne-like	8.5(1)	8.6^p	$8.5(2)^w$
Mg-like	10.8(3)	$10.9(2)^p$	11.03^p
Ar-like	16.6(3)	16.60^w	16.29^w
Ca-like		$18.9(1)^p$	19.0^p
Zn-like		28.9^p	29.0^p
Kr-like		34.57^w	34.27^w
Sr-like		$37.0(1)^w$	$37.2(1)^p$
Cd-like		46.9^w	$47.1(2)^p$
Xe-like		$52.4(4)^w$	$52.3(1)^w$

basis-size dependence up to bases of 30 functions per radial orbital. The stabilized results were obtained for bases of 40–60 functions per radial orbital.

We studied all closed-shell (CS) atomic systems up to xenon-like systems. For heavier atoms, it is better to account for the relativistic effects from the very beginning. Given the extensiveness of the data, we do not present the coefficients for the series (7) and (14) here. Nevertheless, they are available on request. We note that the results obtained from the series (7) are in an excellent agreement with the best results available in the literature [29–31].

The obtained perturbative energies (7) were analyzed by the method described in [32]. We obtained critical nuclear charges that correspond to the lowest value of nuclear charge Z_c (for a given electronic configuration) for which a SAS can still exist. We observed that, within numerical errors, the radii of convergence of total and all orbital energies are the same. However, this method yielded reasonable results only for systems up to Ar-like systems. Even for these systems, the convergence of the method was not impressive, though. This suggests that the assumption on the nature of the closest singularity to the expansion point, which is the basis of the method, is not completely correct; for details see [25].

Next, we constructed the stability matrix, see Sec. II B, for $S = 0, 1$; $L = 0, 1, 2, 3$; and $\Pi = 0, 1$. We then found perturbative series (in $1/Z$) of the lowest eigenvalues $\lambda_{S,L,\Pi}$ of the blocks of the symmetry-adapted stability matrix. We need to sum these series outside their radius of convergence; thus the series were resummed using Padé or Weniger sequence transformations to yield onsets of instabilities $Z_i(S, L, \Pi)$, $\lambda_{S,L,\Pi}(Z = Z_i) = 0$.

A summary of the results displayed in Tables I–IV follows. For illustration, see Fig. 2, where $\lambda_{S,L,\Pi}$ is plotted as a function of Z for Ca-like systems for $S = 1$ and $L = 1, 2, 3$ monoexcitations.

(i) Pure singlet instability: The found onsets of pure singlet $Z_i(0, 0)$ and pure spin $Z_i(1, 0)$ instabilities are listed in Table I. Note, though, that the performance of the Weniger or Padé sequence transformations is not always impressive. First,

TABLE II. Onsets of general instabilities $Z_i(1, L, \Pi)$ for systems isoelectronic with rare-earth metals for $L = 1, 2, 3$; only $Z_i(1, L, \Pi) > Z_i(0, 0)$ are listed. The superscripts w and p denote whether Weniger or Padé summation was used, respectively. The superscripts and subscripts $+, -$ denote the sign of $\lambda_{S,L,\Pi}(Z)$ for Z above or below $Z_i(S, L, \Pi)$, respectively. $-$ means that no solution above $Z_i(0, 0)$ was found.

	$Z_i(1, 1, 1)$	$Z_i(1, 2, 0)$	$Z_i(1, 3, 1)$
Be-like	$^{+}_{-}4.50^w$	$^{+}_{-}2.93^w$	$^{+}_{-}2.88^p$
Mg-like	$^{+}_{-}11.61^p$	$^{+}_{-}11.39^w$	$^{+}_{-}10.94^p$
Ca-like	$^{+}_{-}20.19^p$	$^{-}_{+}20.60^p$	$-$
		$^{+}_{-}19.4^p$	
Sr-like	$^{+}_{-}38.3(1)^w$	$^{-}_{+}38.65^p$	$^{-}_{+}49.49^w$
			$^{+}_{-}38.72^w$

we would like to draw attention to the coincidence (within numerical error) of $Z_i(0, 0)$ and Z_c, i.e.,

$$Z_i(0, 0) = Z_c. \tag{16}$$

Unlike when determining Z_c, we were able to find $Z_i(0, 0)$ for all studied systems. We can see that indeed in all cases (with the possible exception of Sr-like and Xe-like systems, but here we could be still within the error of the sequence transformation), $Z_i(0, 0)$ lies in the interval $(Z_n - 2, Z_n - 1)$; Z_n denotes the nuclear charge for which a given atom is electrically neutral. This means that isolated cations, neutral atoms, and once negatively charged ions do exist in the HF approximation, while doubly negative anions do not. We conclude that the results obtained in [33–35] for O^{2-} (and S^{2-}) are artifacts of finite basis sets [36]. Hence these results are of no relevance to the experimental finding of possible resonances in O^{2-} [37]; cf. [38]. Further, for helium-like atoms, $Z_c^{\text{exact}} \simeq 0.911$ [39]; hence $Z_c^{\text{HF}} = 0.82 < Z_c^{\text{exact}}$. From this example we see that electronic correlation has a destabilizing effect and Z_c^{HF} is a lower bound to Z_c^{exact}. Although we are not aware of any proof that this indeed holds in general, we find it very likely. Thus probably no bound-state solution of the exact Schrödinger equation exists for any double and more negative isolated atomic anions. The nonisolated anions are another story, however; see, e.g., [40–42]. Nevertheless, the double negative anions, even when isolated, can still support resonances. This seems to be the case of O^{2-} and S^{2-} as there is both experimental [37,38,43] and theoretical [44,45]

TABLE III. Onsets of general instabilities $Z_i(1, L, \Pi)$ for systems isoelectronic with noble gases for $L = 1, 2, 3$ and $\Pi = 0, 1$; only $Z_i(1, L, \Pi) > Z_i(0, 0)$ are listed. Meaning of the superscripts w and p, the superscripts and subscripts $+, -$, and $-$ is the same as in Table II.

	$Z_i(1,1,0)$	$Z_i(1,1,1)$	$Z_i(1,2,0)$	$Z_i(1,2,1)$	$Z_i(1,3,0)$	$Z_i(1,3,1)$
He-like		$^{+}_{-}0.93^w$	$^{+}_{-}0.84^p$			$^{+}_{-}0.83^p$
Ne-like	$^{+}_{-}8.84^p$	$^{+}_{-}8.38^w$	$^{+}_{-}8.5^w$	$^{+}_{-}8.93^w$	$^{+}_{-}8.61^w$	$^{+}_{-}8.79^w$
Ar-like	$^{+}_{-}16.30^w$	$^{+}_{-}17.0(4)^p$	$-$	$^{+}_{-}17.5(2)^p$	$^{+}_{-}17.18^w$	$^{+}_{-}17.0(5)^p$
Kr-like	$^{+}_{-}34.29^w$	$^{+}_{-}35.0(2)^p$	$-$	$^{+}_{-}34.83^p$	$^{+}_{-}35.80^w$	$^{+}_{-}34.5(4)^p$
Xe-like	$^{+}_{-}52.16^p$	$-$	$^{-}_{+}59.7(1)^p$	$-$	$^{-}_{+}60.07^p$	$^{-}_{+}62.83^p$

TABLE IV. Onsets of general instabilities $Z_i(1, L, \Pi)$ for systems isoelectronic with Zn and Cd for $L = 1, 2, 3$; only $Z_i(1, L, \Pi) > Z_i(0, 0)$ are listed. Meaning of the superscripts w and p and the superscripts and subscripts $+, -$ is the same as in Table II.

	$Z_i(1, 1, 1)$	$Z_i(1, 2, 0)$	$Z_i(1, 3, 1)$
Zn-like	$^{+}_{-}29.45^w$	$^{+}_{-}28.95^w$	$^{+}_{-}30.49^w$
Cd-like	$^{+}_{-}47.56^w$	$^{+}_{-}46.8(2)^p$	$^{-}_{+}59.64^p$

evidence for it. Another alternative to the methods used in [44,45] would be an extensive configuration interaction accompanied by complex scaling [46]. We would like to return to this question in the future.

(ii) *Pure spin instability*: We found the pure spin instabilities $Z_i(1, 0)$ to lie in the interval $(Z_n - 1, Z_n)$ in the case of rare-earth-metal-, He-, Zn-, and Cd-like systems. This means that for once negative anions of these systems, which still can exist as shown above, a spin BSS lies below the SAS. In the cases of H^- and Li^-, the presence of the BSS manifests itself through a nonconvergence of the SC method for RHF equations. In the case of systems isoelectronic with noble gases, the pure spin instability lies below $Z_i(0, 0)$. That is, the systems cease to exist before a spin instability can appear.

(iii) *Orbital instabilities*: We found that pure orbital instabilities $Z_i(0, L, \Pi)$ are less likely than general instabilities $Z_i(1, L, \Pi)$; we will therefore present and discuss results only for the latter (see Tables II, III, and IV).
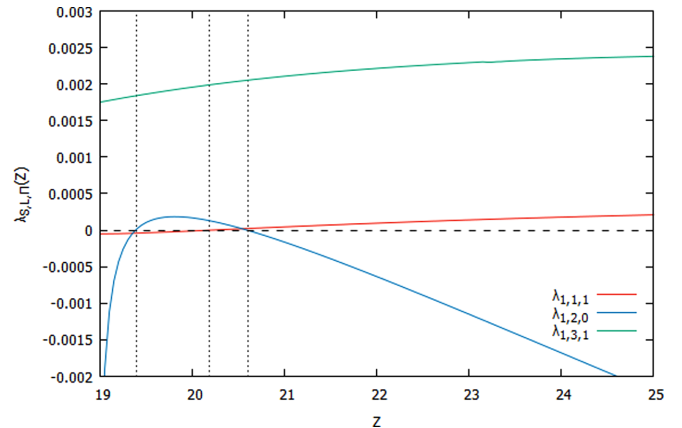

FIG. 2. Dependence of the eigenvalues $\lambda_{S,L,\Pi}$ on the nuclear charge Z for Ca-like systems. The dashed horizontal line highlights $\lambda = 0$. The dashed vertical lines mark where the three curves $\lambda_{S,L,\Pi}$ change their sign and are at $Z = Z_i(1, 1, 1) \simeq 20.19$, $Z = Z_i(1, 2, 0) \simeq 20.60$, and $Z = Z_i'(1, 2, 0) \simeq 19.4$; cf. Table II. Consider the particular case of a neutral calcium atom ($Z = 20$), for instance. The green (the top one for large Z) and blue (the bottom one for large Z) curves lie above $\lambda = 0$; thus we see that the atom is (1,2,0)- and (1,3,1)-stable. The red line (the middle one for large Z) lies below $\lambda = 0$, showing that the atom is (1,1,1)-unstable. By the (1,1,1) instability we mean that the SA HF solution is unstable with respect to the monoexcitations that violate spin ($S = 1$) and orbital ($L = 1$, $\Pi = 1$) symmetry. Similarly, we see that all cations are (1,1,1)- and (1,3,1)-stable, but (1,2,0)-unstable.

The best way is to summarize the behavior of general instabilities according to the sign of λ_0.

First, for $\lambda_0 > 0$ we found that in all studied cases the highest $Z_i(1, L, \Pi)$ lies in the interval $(Z_n - 2, Z_n - 1)$ and there are no other roots above $Z_n - 2$.

Second, if $\lambda_0 < 0$, the highest $Z_i(1, L, \Pi)$ appears above Z_n, and cations with $Z > Z_i(1, L, \Pi)$ are unstable, while systems with $Z < Z_i(1, L, \Pi)$ are stable. In addition, there may be another root $Z_i'(1, L, \Pi)$; $Z_i'(1, L, \Pi) < Z_i(1, L, \Pi)$. Depending on the exact position of $Z_i'(1, L, \Pi)$, the neutral atom may be stable (e.g., Ca with respect to $S = 1, L = 2, \Pi = 0$) or unstable (e.g., Sr with respect to $S = 1, L = 3, \Pi = 1$); see Fig. 2.

The last case, $\lambda_0 = 0$, is the one showing the least characteristic behavior. Generally, $Z_i(1, L, \Pi)$ lies in the interval $(Z_n - 1, Z_n)$ and there are no other solutions for $Z > Z_i(0, 0)$. There are a few exceptions, though. In the case of Be-,Ca-, and Sr-like systems, $Z_i(1, 1, 1) > Z_n$, which thus yields the neutral Be, Ca, and Sr atoms $(1,1,1)$-unstable.

We note that our results for Be-like systems are in agreement with those obtained in [17]. Note, though, that the authors investigated the instability of RHF solution only in the region $Z = 3$–5 and they did not adapt the stability matrix to orbital symmetry.

IV. CONCLUSIONS

Starting with the methodological point of view, the major result of this work is that the onset of the pure singlet instability, i.e., the instability preserving all the symmetries of the underlying Hamiltonian, coincides with the critical charge Z_c, i.e., the smallest charge that still supports a bound-state RHF solution. This gives a physical meaning to the pure singlet instability.

Note, in addition, that the perturbative treatment developed in this paper provides global information about the solution of the HF equations. Indeed, when using the SC method, one can never be sure whether the found solution is truly a global minimum. In contrast to it, when we are in the domain of analyticity, i.e., for $Z > Z_c$, and when the stability matrix is positive definite, the RHF solution is clearly a global minimum; cf. [47]. Note, though, that atoms are clearly extremely simple in this respect as the isoelectronic species are characterized by a single parameter Z. Also, note that in the case of other than pure singlet instability, the HF energy is an *analytic* function of nuclear charge Z in the vicinity of the onset of instability $Z_i(S, L, \Pi)$; the symmetry breaking is not accompanied by any singular behavior of the energy; cf. [48]. Finally, let us note that we established the existence and uniqueness of RHF solutions for closed-shell atoms that are much stronger than those proved rigorously in [49]. It would be interesting to see whether the results of this paper can be put on the same rigorous footing.

On the side of the actual stability of the RHF solutions for closed-shell atoms, the situation is the following.

The critical charge Z_c lies in the interval $(Z_n - 2, Z_n - 1)$; Z_n is the value for which the atom is electrically neutral. This means that no basis-set-independent bound-state RHF solution for any isolated doubly negative atomic anions exists; however, there can be still resonance solutions.

The onset of the pure spin instability $Z_i(1, 0)$ lies in the interval $(Z_n - 1, Z_n)$ in the case of closed shells of s and d elements and of He-like systems, but it is smaller than $Z_n - 1$ for noble-gas-like systems (except for He).

For the onset of general instability $Z_i(S, L, \Pi)$ the following qualitative picture holds. First, not surprisingly, the pure orbital instability appears less likely than the general instability $Z_i(0, L, \Pi) < Z_i(1, L, \Pi)$. Next, depending on the type of the lowest monoexcitation, we can distinguish three cases. Recall that n_{HO} and n_{LU} denote the principal quantum numbers of the occupied orbital with the highest and the virtual orbital with the lowest hydrogenic energies, respectively. First, if $n_{LU} > n_{HO}$, $Z_i(S, L, \Pi) < Z_n - 1$ and all existing systems are stable. Second, if $n_{LU} = n_{HO}$, $Z_i(S, L, \Pi)$ lies in the interval $(Z_n - 1, Z_n + 1)$ and there are no other roots above Z_c. Third, if $n_{LU} < n_{HO}$, $Z_i(S, L, \Pi) > Z_n$ and cations with $Z > Z_i(S, L, \Pi)$ are unstable. There is usually another root $Z_i'(S, L, \Pi) < Z_i(S, L, \Pi)$ and depending on its position, the corresponding neutral atom is (un)stable.

Generally speaking, as long as the shells are filled according to hydrogenic energies, electronic correlation is likely to destabilize the system. However, once this ceases to hold, for instance the $4s$ orbital is filled before the $3d$ orbital, electronic correlation has a tendency to stabilize the system.

There are several loose ends that we would like to investigate in the future. The most interesting are the following. The first and foremost is to answer the question of obtaining a BSS from a SAS; see, e.g., [3,4,7,50,51]. The second is to resolve the question of how to best account for the electronic correlation in the case when HF symmetry breaking takes place. It has long been recognized, see, e.g., [4], that in the case of open-shell systems the spin instability is always present. When dealing with open shells, one usually starts with closed-shell cations to avoid spin contamination; see, e.g., [52]. However, in atoms the situation is not so simple since, as we have shown, moderately heavy cations are not spherically symmetric on the IPM level. The third is to investigate whether factorization of the singlet stability matrix into the pure singlet instability and the instability violating some other than spin symmetry of the Hamiltonian can shed the light on the question of real versus artifactual symmetry breaking on the IPM level. Comparison of the exact and HF critical charges for helium illustrates that, from all the instabilities found, the pure singlet instability is the one that persists even when the electron correlation is taken into account exactly.

[1] By IPM is usually meant a general HF solution, that is, any solution that can be obtained by considering all possible monoexcitations from a SA HF solution see, e.g., [2] or the Nijmegen lectures of J. Paldus, available at http://www.math.uwaterloo.ca/~paldus/resources.html.

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