# HARTREE–FOCK STABILITY AND BROKEN SYMMETRY SOLUTIONS OF $O^{2-}$ AND $S^{2-}$ ANIONS IN EXTERNAL CONFINEMENT

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*We dedicate this paper to the memory of Professor Jaroslav Koutecký, who pioneered the field of quantum chemistry in Czechoslovakia. We shall be forever grateful to him for his steady encouragements and guidance, stimulating discussions, and friendly counsel and help that he extended to us over the years.*

> *All the world's a stage,*
> *And all the men and women merely players:*
> *They have their exits and their entrances;*
> *And one man in his time has many parts …*
>
> Shakespeare, *As You Like It* (1599)

We study the effect of a confining potential on systems that exhibit Hartree–Fock (HF) instabilities, and thus admit broken symmetry (BS) HF solutions, by relying on the $O^{2-}$ and $S^{2-}$ doubly-charged anions as model systems. We find that with the increasing strength of the external harmonic confinement potential, $W(r) = \frac{1}{2}(\omega r)^2$ (with $0.0 \le \omega < 0.2$), the BS solutions are systematically eliminated. We use extended, diffuse, doubly-augmented Gaussian basis sets up to and including d-aug-cc-pV6Z, and find that the number and the character of BS solutions exhibit significant basis set effects. These basis sets were further extended by additional ghost basis functions, located away from the atomic center. The role of the electron correlation effects for the BS HF solutions was examined by the CCSD(T) method. In

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addition to modelling the confinement by the harmonic-like potential $W(r)$, we also examined a more realistic "confinement", realized by a grid of point charges modelling the crystal structure of MgO. Again, we find that the HF instabilities and the implied BS solutions disappear with the increasing magnitude of the model charges simulating the crystal environment. At the same time, the $O^{2-}$ anion is energetically stabilized with respect to both the $O^-$ anion and the neutral oxygen atom.

**Keywords:** Hartree–Fock stability; Broken symmetry solutions; Confined systems; Confining potential; Correlation effects; CCSD(T), $O^{2-}$ and $S^{2-}$ anions; MgO crystal; Ab initio calculations.

During the past decade there has been a growing interest in the study of the behaviour and properties of various atomic and molecular systems that are immersed in an external potential field representing a spatial confinement. This work was in turn stimulated by advances in semiconductor manufacturing processes and by the developments in nanotechnology. One type of such systems is often referred to as quantum dots and quantum wires, or as artificial atoms or molecules. The confinement may also be realized via various nanocavities in mesoscopic objects, such as provided by molecular cages or crystal latices (e.g., clathrates, fullerenes, nanotubes, zeolites, etc.), but also by nanobubbles, as formed in liquid helium and other liquefied inert gases.

Our interest in these systems has arisen from two rather diverse sources, namely from an extensive work on confined systems carried out at the Max Planck Institute for Astrophysics in Garching by Professor Diercksen and his group[1–5], aswell as an older work on the stability of highly charged negative ions[6]. Diercksen's group developed appropriate codes (extended by Sako to study confined systems) and investigated many aspects of confined systems, including their electronic structure[1], and various spectroscopic[2], electric[3], dynamical[4], and other[5] properties. On the other hand, we were particularly interested in a possibility that such a confinement may help to stabilize otherwise unstable, electron-rich systems. For this reason we decided to investigate the effect of a confining potential on a special class of $N$-electron systems, in particular those whose Hartree–Fock (HF) solutions are singlet-unstable, and for which there exist broken-symmetry (BS) solutions in addition to the standard symmetry-adapted (SA) ones[6].

Typical examples of atomic systems which exhibit instabilities and BS solutions are multiply charged anions, i.e., neutral atoms or molecules with additional electrons, as represented, e.g., by doubly negative anions[6] such as $O^{2-}$ and $S^{2-}$. Although such structures have never been observed under normal conditions (see, however, ref.[7]; see also ref.[8]), and thus no experimental data are available for them (see below), they are often postulated as possible intervening – at least as formal – fragments[9] (see also refs[10]) in the analysis of a bonding capacity and strength of various polyoxometalates (POMs). POMs constitute a huge class of metal–oxygen clusters, usually involving Mo, W or V, and have many potential applications in as diverse fields as catalysis, material science, and medicine (see, e.g., refs[9,11]). There exists a vast literature, both experimental and theoretical, concerning these compounds and a multitude of their exploitations is based on their ability to bind one or several electrons while undergoing only a minimal structural changes.

In fact, POMs represent typical host–guest supramolecular structures and are sometimes formulated as clathrate-like structures. In the case of the so-called Lindqvist anions[12], it is precisely the anion $O^{2-}$ that represents the central oxide ion, so that, for example, the Lindqvist-type structures $[M_6O_{19}]^{n-}$ ($n$ = 8 for M = Nb and Ta; $n$ = 2 for M = Mo and W) are represented as a clathrate $O^{2-}@[M_6O_{18}]^{(n-2)-}$ or $[W_{10}O_{32}]^{4-}$ as $O^{2-}@[W_{10}O_{31}]^{2-}$.

In this connection we wish to recall an early formulation of the HF stability conditions[13], and of the issuing BS solutions, for a series of ten-electron atomic systems[6], as described by the LCAO-SCF method based on a minimum basis sets of Slater-type atomic orbitals (AOs). Continuously varying the nuclear charge $Z$ from $Z = 10$ (the neutral Ne atom), to $Z = 9$ (the $F^-$ ion), and, finally, to $Z = 8$, we reach a hypothetical doubly-negative oxide ion $O^{2-}$. Testing for the singlet stability[13] of the resulting solutions, we find[6] that while the SA (i.e., spherically-symmetric, closed-shell, pure singlet) solutions for Ne and $F^-$ are perfectly stable, thus representing a true minimum on the mean-energy hypersurface, the SA solution for $O^{2-}$ is singlet unstable, the instability onset arising at about $Z \approx 8.6$. In fact, once we reach $O^{2-}$, we find several (essentially two, one triply and one quintuply degenerate) negative eigenvalues in the singlet stability problem (of course, the triplet or non-singlet instability arises even slightly earlier, see ref.[6] for details; however, we are interested here in spin-uncontaminated, pure-singlet solutions). Following the direction of steepest descent at the stationary point as given by the corresponding eigenvectors of the stability problem, it was possible to generate BS solutions, one of an oblate and one of a prolate type, referred to as the *D* and *P* solutions, according to the multiplicity of the corresponding root of the stability problem. The *D*-type solution, which is higher in energy and still singlet unstable was found earlier in an ad hoc manner by Prat[14] (see also ref.[15]). This solution leaves the 2p orbitals with $m = \pm 1$ still degenerate, while all three 2p orbitals of the *P*-type solution have distinct orbital energies. It is this latter BS solution of the *P*-type that is singlet stable and has the lowest energy[6].

Now, at first sight, it seems surprising that stationary solutions of either a SA or BS type for $O^{2-}$ exist at all. In fact, the instability of the SA solution, and the existence of the lower-energy BS solutions, indicates the instability of the regular solution having a spherical symmetry and may be interpreted as a tendency of both electrons (since we insist on the closed-shell form of the solution) to escape the nucleus, thus breaking the spherical symmetry. The fact that we do find such solutions for $O^{2-}$ is thus clearly related to the fact that we employ a finite basis set, which will not allow the electrons to "escape". Indeed, when we attempt to compute the SCF solution for $O^{2-}$ by relying on the atomic codes that employ numerical integration of HF equations[16], while enforcing the single-determinantal closed-shell form of the wave function, we encounter convergence difficulties, since both excess electrons try to populate a plane-wave-type orbital, indicating a tendency to escape the anion[17].

In general, we know that the electrostatic potential due to the nuclear charge $Z$ can stabilize an atomic system with $N \le Z$ electrons and in most cases with $N = Z + 1$ electrons, but hardly with two or more excess electrons. Although there seems to be little doubt about the existence of such ions, including $O^{2-}$ and $S^{2-}$, in solid state crystal lattices, there is no evidence of their existence in the gas phase. In spite of various claims to the contrary (see ref.[7]), there exists a firm experimental evidence that no such "long-lived", doubly-charged negative atomic anions exist. For example, using a double-focusing mass-spectrometer Spence et al.[18] did not find any evidence of the existence of such ions with the lifetime exceeding $10^{-5}$ s and, more recently, Chang et al.[19], carried out an ultrasensitive search using a tandem-accelerator-based charge spectrometer with a high-current cesium sputter source and found no positive evidence of such ions while using a detection sensitivity $[O^{2-}]/[O^{-}] \le 1.1 \times 10^{-16}$.

In this paper we wish to demonstrate that the stability of such electron-rich systems can be achieved not only by raising the nuclear charge, but also by immersing them in an external potential field as mentioned earlier. We shall thus investigate the behaviour of the electronically unstable systems $O^{2-}$ and $S^{2-}$ when passing from the system in vacuum to the system in a specific surrounding environment. This environment can be represented, for example, by a suitably selected external confining potential. The main goal of this work is to demonstrate that in the presence of the external confinement, in our case effected by the spherically-symmetric, harmonic-type potential $W(r) = \frac{1}{2}(\omega r)^2$, the HF instabilities and BS solutions that are typical for electron-rich systems, may be avoided. We will also study the $O^{2-}$ anion within a more realistic confinement potential modelling the crystal lattice. Our choice will be an electrostatic point charge potential[20], in which the behaviour of the $O^{2-}$ anion may approach that of a realistic environment, in which the system may be stabilized enough so as to actually bind the two extra electrons.

## STABILITY OF HARTREE-FOCK SOLUTIONS

### *Basic Concepts*

The HF approximation strives for the energetically optimal, independent-particle-model (IPM) wave function by relying on the variation principle

$$E(\Phi) \leq \langle \Phi | H | \Phi / \langle \Phi | \Phi \rangle \ . \qquad (1)$$

In cases considered here, $|\Phi\rangle$ represents a closed-shell, single antisymmetrized product (or single-determinantal), trial wave function, built from spin-orbitals $|A\rangle = |a^{\pm}\rangle$. Moreover, we use a finite basis set to express one-electron orbitals $|a\rangle$ as a linear combination of basis set atomic orbitals (AOs) $|\phi_i\rangle$ (LCAO approximation), the LCAO coefficients representing the variational parameters. The HF equations that warrant the vanishing of the first variation $\delta^{(1)}E(\Phi)$ of the mean-energy functional (*1*),

$$\delta^{(1)}E(\Phi)|_{\Phi=\Phi_0} = 0 \ , \qquad (2)$$

do not guarantee that their solution corresponds to an absolute or, in fact, even to a local minimum on the energy hypersurface $E(\Phi)$, but only that it represents a stationary point. Moreover, these equations, being highly nonlinear, may possess a multitude of solutions[21].

Although in the majority of cases the standard SCF solution, preserving the symmetry of the Hamiltonian considered, does represent a bona fide solution associated with the absolute energy minimum, there are many cases where this is not the case, and where the relaxation of the symmetry restrictions leads to a solution or solutions with a lower energy. This observation is the content of the well-known “symmetry dilemma”, first formulated by Löwdin[22]. Clearly, the exact wave function $|\Psi\rangle$ must represent a simultaneous eigenstate of both the Hamiltonian $H$ and of all the operators $\Lambda_k$ that commute with $H$. The operators $\Lambda_k$ describe the invariance of $H$

with respect to various symmetries (spin, spatial, time-reversal, total electron number, etc.) and constitute an appropriate symmetry group or groups. The requirement that the variational trial wave function $|\Phi\rangle$ also possesses these symmetries (i.e., that it is a simultaneous eigenfunction of $H$ and of the corresponding $\Lambda_k$ operators) represents an imposition of additional constraints on $|\Phi\rangle$, leading to a constrained variational problem. However, such constraints can only raise the energy, since they restrict the available variational space. Thus, breaking one or more such symmetries can lead to BS solutions with lower energy.

Most often it is the breaking of the total spin that can produce a lower-energy unrestricted HF (UHF) solution of the different orbitals for different spins (DODS) type. This is in fact always the case for open-shell systems due to an imbalance between the up and down spins in the IPM determinant, but the occurrence of UHF solutions for closed-shell systems is rather rare. In fact, Koutecký was one of the first to describe such solutions[23].

In order to ascertain that a given HF solution is associated with an energy minimum, we have to evaluate the second variation of the energy functional (*1*) or the Hessian $\delta^{(2)}E(\Phi)$ at $|\Phi_0\rangle$, and to check for its positive definiteness. Of course, even when $E(\Phi_0)$ represents a true minimum, there is no guarantee that this is an absolute minimum (see, e.g., refs[24–26]). The general stability conditions were first formulated by Thouless[27]. The specification of these conditions for closed-shell systems[13] led to the introduction of the concepts of the singlet and triplet (or non-singlet) (in)stabilities, and to the formulation of the corresponding singlet and triplet stability conditions. These concepts were later generalized to doublet stability conditions for simple open shells[28], as well as to other types of symmetry breaking (for an overview and unification of various stability conditions, see refs[25,26]).

### *Basic Formalism*

We next present a brief formulation of the working equations for HF stability conditions in order to fix the terminology and outline the formalism employed. The reader is referred to the original literature[13] or to more recent reviews[25,26].

Labeling the generic, occupied, and unoccupied spinorbitals by capitals $I,J,K,L,\ldots$, $A,B,C,\ldots$, and $R,S,T,\ldots$, respectively, and the corresponding orbitals by the corresponding lower-case letters, we can express the $N = 2n$ electron closed-shell IPM wave function $|\Phi_0\rangle$ as follows

$$|\Phi_0\rangle = \left( \prod_{A=A_1}^{A_N} X^{\dagger}_{A_i} \right) |0\rangle = |\{A_1 A_2 \ldots A_N\}\rangle = |\{a_1^+, a_1^-, a_2^+, \ldots a_n^+, a_n^-\}\rangle \qquad (3)$$

where $X_I^{\dagger}$ and $X_I$ designate the creation and annihilation operators associated with the spin orbital $I = i^+$ or $I = i^-$, the superscripts + and – indicating the spin-up or spin-down eigenstates of $S_z$, $|0\rangle$ represents a vacuum state, and the curly brackets imply the antisymmetrization. According to Thouless' theorem[27], an arbitrary single antisymmetrized product (IPM or determinantal) wave function $|\Phi\rangle$ that is not orthogonal to $|\Phi_0\rangle$, can be expressed in the following intermediately normalized form

$$|\Phi\rangle = \exp(C_1)|\Phi_0\rangle \qquad (4)$$

where $C_1$ designates a monoexcitation operator

$$C_1 = c_R^A e_A^R, \qquad e_A^R = X_R^{\dagger} X_A. \qquad (5)$$

Here, as in the following text, we assume the summation convention over repeated indices.

It is not difficult to find the expression for the second variation of the mean-energy functional, Eq. (*1*), (using, for example, a diagrammatic technique[25])

$$\delta^{(2)}E = \left\| \begin{matrix} \mathbf{C} \\ \overline{\mathbf{C}} \end{matrix} \right\|^{\dagger} \left\| \begin{matrix} \mathbf{A} & \mathbf{B} \\ \overline{\mathbf{B}} & \overline{\mathbf{A}} \end{matrix} \right\| \left\| \begin{matrix} \mathbf{C} \\ \overline{\mathbf{C}} \end{matrix} \right\| \qquad (6)$$

where we defined matrices

$$\mathbf{C} = \left\| c_R^A \right\|, \qquad \mathbf{A} = \left\| A_{RS}^{AB} \right\|, \qquad \mathbf{B} = \left\| B_{RS}^{AB} \right\| \qquad (7)$$

with matrix elements

$$A_{RS}^{AB} = \langle R|f|S\rangle\langle B|A\rangle - \langle B|f|A\rangle\langle R|S\rangle + \langle RB|v|AS\rangle_a$$

$$B_{RS}^{AB} = \langle RS|v|AB\rangle_a. \qquad (8)$$

Here, the rows and columns are labeled by monoexcitation labels $\binom{A}{R}$ or $\binom{B}{S}$, the subscript "*a*" implies the antisymmetrized two-electron integral, and $\langle I|f|J\rangle$ represents the matrix element of the Fock operator, i.e.,

$$\langle IJ|v|KL\rangle_a = \langle IJ|v|KL\rangle - \langle IJ|v|LK\rangle \tag{9}$$

$$\langle I|f|J\rangle = \langle I|h|J\rangle + \sum_A \langle IA|v|JA\rangle_a \tag{10}$$

For spin-independent electronic Hamiltonian

$$H = h^j_i E^i_j(0) + v^{jl}_{ik}[E^i_j(0)E^k_l(0) - \delta^k_j E^i_l(0)] \tag{11}$$

where now $v^{jl}_{ik} = \langle jl|v|ik\rangle$ and $E^i_j(0)$ represents a spin-free unitary group generator

$$E^i_j(\kappa) = e^{i^+}_{j^+} + (-1)^\kappa e^{i^-}_{j^-} \qquad (\kappa = 0, 1) \tag{12}$$

the matrix elements of **A** and **B** matrices become

$$A^{ab}_{rs}(\kappa) = f^r_s\delta^b_a - f^b_a\delta^r_s + 2\delta_{\kappa,0}v^{rb}_{as} - v^{rb}_{sa}$$

$$B^{ab}_{rs}(\kappa) = 2\delta_{\kappa,0}v^{ab}_{rs} - v^{ab}_{sr} \tag{13}$$

with the parameter κ referring to the singlet (κ = 0) and triplet (κ = 1) coupling and, correspondingly, singlet and triplet (non-singlet) stability problem, namely

$$\begin{Vmatrix} \mathbf{A}(\kappa) & \mathbf{B}(\kappa) \\ \overline{\mathbf{B}}(\kappa) & \overline{\mathbf{A}}(\kappa) \end{Vmatrix} \begin{Vmatrix} \mathbf{D}_i(\kappa) \\ \overline{\mathbf{D}}_i(\kappa) \end{Vmatrix} = \lambda_i \begin{Vmatrix} \mathbf{D}_i(\kappa) \\ \overline{\mathbf{D}}_i(\kappa) \end{Vmatrix} \qquad (\kappa = 0, 1)\,. \tag{14}$$

Note that this is a Hermitian eigenvalue problem, since **A** is hermitian and $\mathbf{B}^\dagger = \overline{\mathbf{B}}$. Further, for a standard HF-SCF solution, the matrix elements of the Fock operator are diagonal and are given by the orbital energies $\epsilon_i = \langle i|f|i\rangle$,

$$f_j^i = \epsilon_i \delta_{ij}. \qquad (15)$$

For a HF solution to be stable, all the eigenvalues must be positive, while a negative eigenvalue implies instability, the corresponding eigenvector providing the direction of the steepest descent at $|\Phi_0\rangle$. Moreover, when **A** and **B** are real, as is the case in most applications, the eigenvalue problems (*14*) factorize into the "plus" and "minus" subproblems[13], i.e.,

$$[\mathbf{A}(\kappa) \pm \mathbf{B}(\kappa)]\mathbf{E}_i^{\pm}(\kappa) = \lambda_i^{\pm}(\kappa)\mathbf{E}_i^{\pm}(\kappa), \qquad \mathbf{E}_i^{\pm}(\kappa) = \mathbf{D}_i(\kappa) \pm \overline{\mathbf{D}}_i(\kappa). \qquad (16)$$

## MODEL CONFINING POTENTIALS

During the last decade a number of authors[1–5,29–31] studied various molecular systems trapped in different types of confining potentials. Here we shall employ two different types of confinement: via a spherical, harmonic-oscillator-type potential that is centered on the nucleus, and via a potential that is produced by a set of alternating point charges localized around the system and forming a cubic grid.

### *Spherical Harmonic-Oscillator-Type Confining Potential*

The potential used in this study is represented by an $N$-electron interaction potential $W(r)$ of the spherical, harmonic-oscillator kind[1–3], defined by the sum of one-electron contributions $w(r_i)$,

$$W(r) = \sum_{i=1}^{N} w(r_i) \qquad (17)$$

where, in general, the one-particle potential $w(r_i)$ is represented via a linear combination of powers in electron coordinates

$$w(r_i) = \frac{1}{2} \sum_{t=x_i, y_i, z_i} \omega_t^{n_t+1} (t - b_t)^{2n_t} \qquad (18)$$

with $r_i = x_i, y_i, z_i$. Choosing the parameters as follows: $n_x = n_y = n_z = n = 1$, $b_x = b_y = b_z = b = 0$, and $\omega_x = \omega_y = \omega_z = \omega$, the potential (*18*) results in an isotropic, harmonic-oscillator potential that is centered at the origin of the coordinate system, i.e.,

$$w(r_i) = \frac{1}{2}\omega^2 r_i^2 \, . \tag{19}$$

The spherically symmetric shape of such a potential is useful as a model potential for a confinement of atoms or molecules by external surrounding environment (as, e.g., in zeolites, fullerenes, nanotubes, or quantum dots). One should keep in mind, however, that – in contrast to real systems – such potential represents only a crude model in view of its infinitely high energy barrier.

### *Cubic Point-Charge Grid*

Another, more realistic type of a confining potential is represented by a specific distribution of point charges around the studied system. In our case, we employ a set of alternating point charges $\pm q$ that are located in the nodal points of a cubic grid, having the cell constant $l$, representing the distance between charges, while the studied anion is located in the center of the grid. Our model consists of five layers, each with $5 \times 5 = 25$ alternating point charges, with only the central layer having 24 point charges, since the studied system is located in the center of the cube. Point charges in the six positions closest to the center have a sign opposite to the studied system (i.e., in our case $+q$). This is the simplest model that preserves both the neutrality of the grid and the systematic alternation of positive and negative charges in the grid. Altogether, it consists of $4 \times 25 + 24 = 124$ point charges, and the overall charge of the entire model is the same as the charge of the unconfined system.

We note that this type of a grid is often used as the simplest model that simulates the crystal environment: see, e.g., ref.[20]. The cell constant $l$ of the cubic grid that was used in our study was taken from the MgO crystal, namely $l = 3.976$ a.u.

## RESULTS AND DISCUSSION

The analysis of the stability of HF solutions follows the work of Čížek and Paldus[13] (for an overview of more recent developments, see refs[25,26]), as implemented in the system of computer codes MOLCAS, version 5.4. All results presented below were obtained using MOLCAS 5.4 program package[32]. In CCSD(T) calculations, 1s electrons were kept frozen.

### *Symmetry-Adapted and Broken-Symmetry Solutions for $O^{2-}$*

Doubly negative charged oxygen atom is a system with the negative electron affinity, i.e. the second electron is not bound to $O^-$. The HF solution for the $O^{2-}$ anion exhibits various instabilities, implying the existence of BS solutions that were already described 20 years ago[6]. With the minimum STO basis set[6], one finds three triplet and two singlet instabilities, the third negative root of the triplet instability problem being identical with the lowest root of the singlet type. The latter is triply degenerate, while the second negative singlet instability root is quintuply degenerate. By following the direction implied by the eigenvectors corresponding to the negative singlet instability eigenvalues, two distinct types of BS solutions can be found. These were referred to as the *P*- and *D*-type BS solutions[6], respectively, according to the degeneracy of the corresponding eigenvalue of the stability problem. The *D*-type solution is characterized by the degenerate negative p-orbital energies $\epsilon_{pm}$ for $m = \pm1$ and a positive $\epsilon_{p0}$, while for the *P* solution, all three orbital energies $\epsilon_{pm}$ are different, one of them being again positive.

In the following we shall rely on standard, augmented (aug) correlation-consistent (cc) basis sets[33]. Moreover, we shall augment these standard basis sets by off-center basis functions. We note that the SA solutions for the $O^{2-}$ system, as obtained with these basis sets, exhibit only the quintuple degeneracy of the negative eigenvalues of the Hessian and the degeneracy of the 2p orbital energies with $m = \pm1$. We can thus use the same notation as in ref.[6] and label the BS solutions associated with the quintuply degenerate singlet instability negative eigenvalues as the *D*-type solutions. Such solutions are likely to be unstable to the (total) spin-symmetry breaking, implying that a lower energy UHF solution (of the DODS type) may exist. However, we are interested here only in spin uncontaminated pure-singlet solutions.

### *Basis Set Dependence of SCF Solutions for $O^{2-}$*

When searching for HF solutions of the $O^{2-}$ anion, the SCF procedure leads to two distinct solutions, depending on the trial wave function employed. One solution is a standard (space and spin) SA solution with triply degenerate 2p orbitals. This solution results when we employ as the initial approximation orbitals that are typical of the $^1S$ state of the $O^{2-}$ anion. In order to access the second solution having a BS, we simply break the degeneracy of the 2p orbitals. In our approach we have employed as the starting orbitals those characterizing the $^1D$ excited state of the neutral oxygen atom, with the occupancy $1s^2\,2s^2\,2p_x^2\,2p_y^2$. Using such starting orbitals, we were able to converge to a BS solution of the $O^{2-}$ anion.

### $O^{2-}$ in Standard, Anion-Centered Basis Sets

When we employ standard *m*-tuply augmented, correlation-consistent *m*-aug-cc-pV*X*Z basis sets[33], we find many similarities to the results obtained with the minimal STO-type basis[6]. Yet, both descriptions are quite different in several aspects. Generally, we find a significant dependence of the studied quantities, such as orbital energies or HF stability roots, on the quality of the basis set employed, in spite of the fact that we use a rather large basis sets. In Table I we summarize the 2p orbital energies for the isoelectronic $F^-$ and $O^{2-}$ anions. For $F^-$, whose HF solutions are singlet-stable, the orbital energies $\epsilon_{2p}$ are completely converged (to within the required accuracy) already at the d-aug-cc-pV*X*Z basis set level with $X = 4$ or 5. This is not the case for the $O^{2-}$ anion, in which case we observe non-negligible differences in the $\epsilon_{2p}$ orbital energies that are associated with the SA solutions even for as large basis sets as those with $X = 4$, 5, and 6. For BS solutions, the values of the $\epsilon_{2p}$ orbital energies vary even more widely with

TABLE I
Orbital energies (in a.u.) of the $O^{2-}$ and $F^-$ anions for symmetry-adapted (SA) and broken-symmetry (BS) solutions, as obtained with different Gaussian-type basis sets.

| Anion | Basic set | SA | BS[a] | |
|---|---|---|---|---|
| | | $\epsilon_{2px} = \epsilon_{2py} = \epsilon_{2pz}$ | $\epsilon_{2px} = \epsilon_{2py}$ | $\epsilon_{2pz}$ |
| $F^-$ | d-aug-cc-pVQZ | –0.1818 | – | – |
| | d-aug-cc-pV5Z | –0.1818 | – | – |
| $O^{2-}$ | d-aug-cc-pVQZ | 0.1171 | –0.1719 | 0.1415 |
| | d-aug-cc-pV5Z | 0.1126 | –0.1937 | 0.1337 |
| | d-aug-cc-pV6Z | 0.0973 | –0.2564 | 0.1108 |
| $O^{2-}$ | C-STO[b] | 0.1254 | –0.1318 | 0.1540 |
| | H-STO[b] | 0.0656 | –0.3101 | 0.0770 |

[a] BS solutions for $O^{2-}$ were obtained using the occupied orbitals of neutral oxygen $1s^2 2s^2 2p_x^2 2p_y^2$ as the initial guess. No BS solutions were found for $F^-$. [b] Ref.[6]

the size of the basis set employed, and are far from reaching the complete basis set (CBS) limit. A similar behaviour was observed earlier[6] for the two distinct basis sets, labeled as C and H bases, which led to a significant difference between the orbital energies as well (see Table I).

The role played by the basis set is even more evident when analyzing the HF stability roots (Table II). For the aug-cc-pVQZ basis, we do not find any negative roots in the singlet instability problem, while the triplet problem yields two negative roots. Only when we include more diffuse basis func-

TABLE II
SCF total energies (in a.u.) and the negative eigenvalues of the singlet (in bold face) and triplet stability problems, classified by the irreps of the $D_{2h}$ point group[a], for the symmetry-adapted solution of $O^{2-}$, as obtained with different Gaussian-type basis sets

| Basis set | SCF energy | $a_g$ | $b_{1g}$ | $b_{2g}$ | $b_{3g}$ |
|---|---|---|---|---|---|
| aug-cc-pVQZ | –74.46201535 | –0.07745 | | | |
| | | –0.01340 | –0.01340 | –0.01340 | – |
| | | –0.01340 | | | |
| d-aug-cc-pVQZ | –74.48696261 | **–0.05517** | **–0.05517** | **–0.05517** | **–0.05517** |
| | | **–0.05517** | | | |
| | | –0.15594 | | | |
| | | –0.11059 | –0.11059 | –0.11059 | –0.11059 |
| | | –0.11059 | | | |
| d-aug-cc-pV5Z | –74.48934618 | **–0.06018** | **–0.06018** | **–0.06018** | **–0.06018** |
| | | **–0.06018** | | | |
| | | –0.15966 | | | |
| | | –0.11510 | –0.11510 | –0.11510 | –0.11510 |
| | | –0.11510 | | | |
| t-aug-cc-pV6Z | –74.51161754 | **–0.10521** | **–0.10521** | **–0.10521** | **–0.10521** |
| | | **–0.10521** | | | |
| | | –0.19699 | | | |
| | | –0.15813 | –0.15813 | –0.15813 | –0.15813 |
| | | –0.15813 | | | |

[a] For computational reasons, only the Abelian subgroup $D_{2h}$ of the rotation group is employed, with the principal axis oriented along the *z*-axis. See the text for details.

tions in the doubly augmented d-aug-cc-pVQZ basis set the SA HF solution becomes singlet-unstable. Further enlargement of the basis set up to and including the t-aug-cc-pV6Z basis does not bring about any qualitative changes (Table II), even though the absolute value of the instability roots and of the total energies increases with the size of the basis set employed. However, we can expect a much more profound dependence on the basis set size for BS solutions, since they are characterized by orbitals with an electron distribution localized far apart from the nucleus[6], so that their proper description requires more extensive and very diffuse basis sets.

In summary, $F^-$ and $O^{2-}$ anions exhibit a similar behaviour to that found earlier with a minimum STO basis set[6]. However, no basis set used here yields singlet and triplet triply degenerate instability roots leading to the *P*-type HF solutions. Thus, with the basis sets employed here, we were able to find only the *D*-type BS solutions.

### *Externally Confined $O^{2-}$ and $S^{2-}$ Anions*

An external confining potential in which the anions are submerged has a profound influence on the eigenvalues of the stability problems. The dependence of the negative eigenvalues $\lambda_k$ corresponding to the singlet-stability problem as a function of the confining potential $\omega$ for the $O^{2-}$ anion is shown in Fig. 1. With the increasing strength of the confining potential, the negative eigenvalues gradually disappear. Quintuply degenerate singlet instability root is the first one to turn positive at $\omega \approx 0.04$. For higher values of $\omega$, only triplet-type HF instabilities remain. Further increase in the strength of the confining potential leads eventually to the disappearance of both quintuply degenerate and nondegenerate triplet instabilities. For $\omega \geq 0.09$ there are no negative eigenvalues in either the singlet or triplet instability problem, implying disappearance of BS solutions, at least BS solutions of the type implied by the singlet instability. In the case of $S^{2-}$ (Fig. 2), the system is more stable in terms of the HF stability thanks to the higher nuclear charge[6]. Negative eigenvalues of the Hessian have smaller absolute values and disappear earlier. The $S^{2-}$ anion becomes stable for $\omega \approx 0.04$.

### *$O^{2-}$ with Off-Center Ghost Basis*

It was shown earlier[6] that the $p_0$ orbital of the *D*-type BS solution has two maxima in the radial charge distribution. The second one is in the region of about 10–12 a.u. Considering this fact and our finding that the BS solutions are very sensitive to the choice of the basis set, we decided to extend our

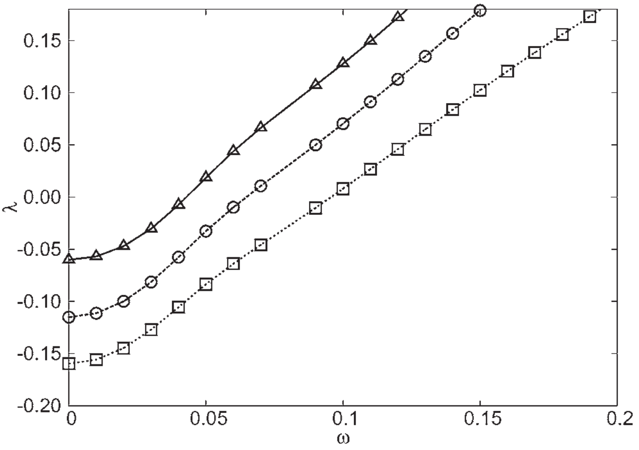

FIG. 1
Negative eigenvalues λ of the singlet and triplet stability problems of the $O^{2-}$ anion as a function of the confining potential strength parameter ω: 5× degenerate singlet instability (△), 5× degenerate triplet instability (○), nondegenerate triplet instability (□). Obtained using the d-aug-cc-pV5Z basis set

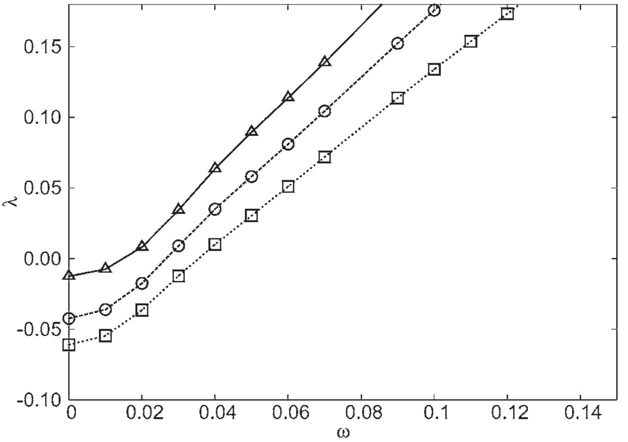

FIG. 2
Negative eigenvalues λ of the singlet and triplet stability problems for the $S^{2-}$ anion as a function of the confining potential strength parameter ω: 5× degenerate singlet instability (△), 5× degenerate triplet instability (○), nondegenerate triplet instability (□). Obtained using the d-aug-cc-pV5Z basis set

bases by supplementing them with additional ghost basis functions, located away from the anion nucleus. A similar idea of a better description of the region away from the center was employed for the $O^{2-}$ anion by Hogreve[15]. An ultimate goal is thus to improve the diffuse part of the standard, augmented, nucleus-centered basis sets in such a way as to enable a more detailed and consistent analysis of HF instabilities and of corresponding BS solutions.

For this purpose, we extended our basis sets by two types of ghost basis functions. The first type is obtained by placing additional basis functions at a distance $\pm R_z$ from the anion nucleus along the $z$-axis. Such a basis set extension leads, of course, to an asymmetric basis set that primarily improves the description of the occupied $2p_z$ orbital. The use of such an asymmetric basis set leads automatically to BS solutions, independently of whether we use the $^1S$-type wave function of $O^{2-}$ as a starting approximation or the $^1D$ wave function of the oxygen atom. We note that this type of basis set extension also makes it possible to exploit standard quantum chemistry codes for a study of certain aspects of HF instabilities, obviating the necessity of writing new programs. For the same reason we employ only the Abelian subgroup $D_{2h}$ of the rotation group to factorize and classify the stability subproblems.

The second type of a basis set extension via off-center basis functions strives to improve the standard, nucleus-centered basis sets, while preserving the symmetry of the problem. In this case the ghost functions are located in all three Cartesian directions, thus improving the $2p_x$, $2p_y$, $2p_z$ functions in the same manner. We refer to such bases as the symmetric, ghost-orbital basis sets. The use of such out-of-center ghost functions is, in fact, a common practice in a number of quantum chemical applications.

### BS Solutions for $O^{2-}$ Using an Asymmetric Ghost-Orbital Basis Set

In the simplest case, we add to our standard basis external basis functions, consisting of an sp set of aug-cc-pVQZ functions, and position them along the $z$-axis at the distance $\pm R_z$ from the origin, where our anion is located. In this way we generate a BS solution by virtue of the basis set asymmetry. For a system whose HF solutions are stable, we expect the asymmetrically added functions to improve the description of occupied orbitals, the effect monotonically abating with the increasing distance $R_z$ along the $z$-axis. This is, for example, the case for $F^-$, shown in Fig. 3. However, for $O^{2-}$, we find a much more interesting behaviour, as seen in Fig. 4. Here we observe

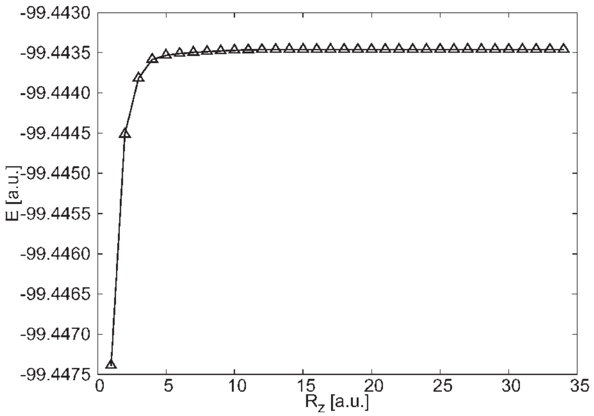

FIG. 3

SCF energy $E$ of the symmetry-adapted solutions for the $F^-$ anion obtained with an asymmetric ghost-orbital basis set (see the text for details) as a function of the distance $\pm R_z$ along the $z$-axis where the ghost orbitals are located. The ghost-orbital basis consists of the aug-cc-pVQZ basis on $F^-$ augmented by the 13s6p/7s6p contracted functions which represent a part of the aug-cc-pVQZ basis set of oxygen. These supplementary basis set functions serve as the off-center (ghost) functions

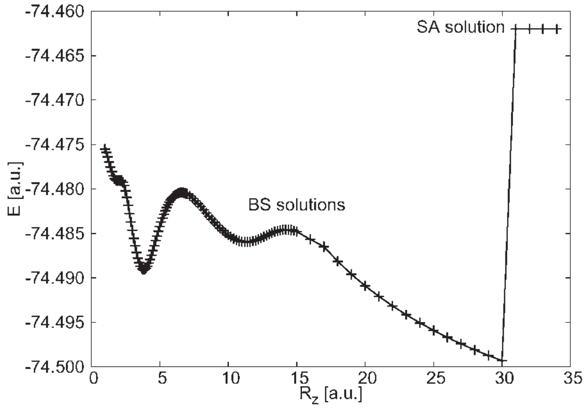

FIG. 4

SCF energy $E$ of the broken-symmetry solutions for the $O^{2-}$ anion obtained with an asymmetric ghost-orbital basis set (see the text for details) as a function of the distance $\pm R_z$ along the $z$-axis where the ghost orbitals are located. The ghost-orbital basis consists of the aug-cc-pVQZ basis on $O^{2-}$ augmented by the 13s6p/7s6p contracted functions which represent a part of the aug-cc-pVQZ basis set of oxygen. These supplementary basis set functions serve as the off-center (ghost) functions a non-monotonic energy dependence on $R_z$ for the *D*-type BS solution. The curve shown in Fig. 4 exhibits several minima, the number of which depends on the nature of the ghost basis employed. First part of the curve, up to about $R_z \approx 3–4$ a.u., might be due to similar effects as found for $F^–$, and could be avoided via a procedure akin to the BSSE (basis set superposition error) correction. This is, however, difficult to accomplish, since we were unable to generate SA solutions up to $R_z = 30$ a.u. Nonetheless, the part of the curve for $R_z \leq 30$ a.u. demonstrates an interesting behaviour of the *D*-type BS solutions. Localization of the remote electron density maximum in the $p_0$ orbital seems to prefer several specific $R_z$ distances. The part of the curve up to about $R_z \approx 30$ a.u. may thus be viewed to represent an escape of $p_0$ electrons from the oxygen anion. Comparing the absolute values of the energy of the SA solution for $O^{2–}$, as obtained with the standard aug-cc-pVQZ basis set (Table II), with that calculated in the same basis supplemented by the ghost functions located at distances larger than 30 a.u. along the *z*-axis (see Fig. 4), implies the absence of any significant interaction of the ghost functions with the basis set centered at the nucleus.

It is also interesting to examine the effect of confinement of varying strength on the energy dependence of BS solutions as a function of the ghost orbital location given by $R_z$. This effect of the spherical, harmonic-type confinement, whose strength is characterized by the parameter ω, on both the SCF and CCSD(T) energies of $O^{2–}$, is shown in Figs 5 and 6, respectively. The curve corresponding to $\omega = 0.0$ is the same one as that in Fig. 4. When ω is switched on, we observe significant changes in the shape of the energy dependence on $R_z$. As may be expected, the region of the curve representing the localization of $p_0 \equiv p_z$ electrons away from the nucleus is rapidly smoothed out, since the spherical, harmonic-type confinement disfavours the escape of an electron to regions of space far from the nucleus. With the increasing strength of the confining potential, also the other minima on the energy curve systematically attenuate, and for large enough ω values, only SA solutions represented by a plateau in Fig. 5 can exist. When we account for the correlation effects via CCSD(T), the shape of the energy dependence on $R_z$ for $\omega = 0.0$ is modified, replacing, or at least suppressing, some of the minima. Nonetheless, a non-monotonic character of this dependence remains unchanged. The general picture of the disappearance of BS solutions with the increasing strength of the confining potential remains the same at the CCSD(T) level (see Fig. 6).

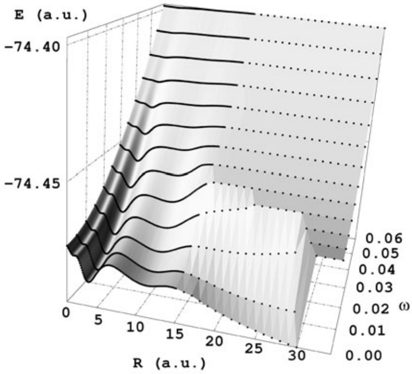

FIG. 5
Total SCF energies *E* of the broken-symmetry solutions for the $O^{2-}$ anion as a function of the distance ±*R* along the *z*-axis where the additional auxiliary out-of-center basis functions are located, for different values of the confining potential strength parameter ω ($0 \leq \omega \leq 0.06$). The asymmetric ghost-orbital basis consisted of the aug-cc-pVQZ basis set on $O^{2-}$ and of the 13s6p/7s6p contracted functions from the aug-cc-pVQZ basis set of oxygen as the off-center (ghost) functions. See the text for details

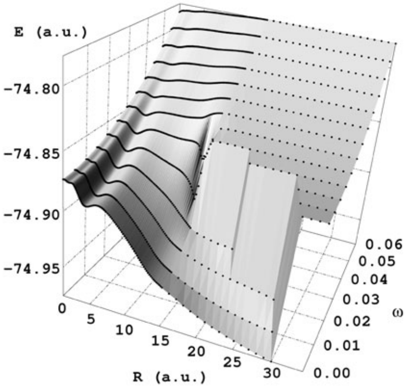

FIG. 6
Total CCSD(T) energies *E* of the broken symmetry solutions for the $O^{2-}$ anion as a function of the distance ±*R* along the *z*-axis where the additional auxiliary out-of-center basis functions are located, for different values of the confining potential strength parameter ω. The asymmetric ghost-orbital basis consisted of the aug-cc-pVQZ basis set on $O^{2-}$ and of the 13s6p/7s6p contracted functions from the aug-cc-pVQZ basis set of oxygen as the off-center (ghost) functions. See the text for details

### BS Solutions for $O^{2-}$ Using a Symmetric Ghost-Orbital Basis Set

We shall now briefly describe another type of HF solutions for $O^{2-}$ that were obtained with basis sets symmetrically extended by off-center ghost functions. Thus, the additional ghost functions are located along the three Cartesian axes $x$, $y$, and $z$ at the same distance $\pm R \equiv \pm R_x = \pm R_y = \pm R_z$. The basic characteristics for three different types of HF solutions obtained with such a basis set are described in Table III. The simplest case is represented

TABLE III
SCF total energies (in a.u.) and the negative eigenvalues of the singlet (in bold face) and triplet stability problems for the symmetry-adapted (SA) and broken-symmetry (BS) solutions of $O^{2-}$, as obtained with the symmetric ghost-orbital basis set[a] (the off-center basis functions were located 11.0 a.u. from the origin along the $x$, $y$, and $z$ axes)

| Solution | SCF energy | $a_g$ | $b_{1g}$ | $b_{1u}$ | $b_{2g}$ | $b_{3g}$ |
|---|---|---|---|---|---|---|
| SA[b] | –74.47071385 | **–0.02530** | **–0.02924** | | **–0.02924** | **–0.02924** |
| | | **–0.02530** | | | | |
| | | –0.12226 | | | | |
| | | –0.07982 | –0.07398 | | –0.07398 | –0.07398 |
| | | –0.07982 | | | | |
| BS[b] | –74.48586154 | | | **–0.01835** | **–0.02078** | **–0.02078** |
| | | | | **–0.01684** | | |
| | | –0.24980 | | –0.06458 | –0.09611 | –0.09611 |
| | | | –0.01870 | –0.01750 | –0.01750 | |
| | | | –0.01687 | | | |
| BS[c] | –74.49453699 | –0.22379 | | | | |
| | | –0.10997 | | | | |
| | | –0.10997 | | | | |
| | | –0.02700 | | | | |
| | | –0.02151 | | | | |
| | | –0.02151 | | | | |
| | | –0.01683 | | | | |
| | | –0.01683 | | | | |

[a] The symmetric ghost-basis set consists of the d-aug-cc-pV5Z basis set on the $O^{2-}$ anion and of the 13s/7s contracted functions from aug-cc-pVQZ basis of oxygen as the off-center (ghost) functions. [b] SA and BS solutions were computed using the $D_{2h}$ point group as the symmetry group. For BS solutions, the occupied orbitals $1s^2 2s^2 2p_x^2 2p_y^2$ of the neutral oxygen atom were employed as the initial guess. [c] BS solution computed using the occupied orbitals $1s^2 2s^2 2p_x^2 2p_y^2$ of the neutral oxygen atom without invoking any symmetry.

by the SA solution. We classify the negative roots of its singlet and triplet stability problems by the irreducible representations (irreps) of the $D_{2h}$ point group (taking the $z$-axis as the principal axis). For the SA solution, the negative roots are found in the totally symmetric as well as in other irreps.

Focusing our attention on the singlet-type instabilities implied by the negative roots appearing in the totally symmetric irrep, we can obtain BS solutions that preserve both the space (dihedral) and spin symmetry. This yields a special type of quasi-symmetric BS solution, which has lower energy than the standard SA solution and is characterized by the energetically-split 2p set of orbitals. Such solution possesses several characteristic features of BS solutions, even though it is not associated with a true energy minimum, but only with a stationary point. It preserves the singlet spin multiplicity, but has a negative root in the singlet stability problem associated with other than totally symmetric irrep.

When we remove singlet instabilities in all irreps, we get a real BS solution preserving the singlet character with even lower HF energy than the just mentioned SA and BS ones. This solution possesses only triplet-type instabilities. In other words, all the pure singlet BS solutions we find may be still triplet-unstable. Nonetheless, the spatial symmetry of this solution has only $C_1$ symmetry (i.e., its symmetry is lowered from $D_{2h}$ to $C_1$), and the corresponding orbitals represent a real mixture of basis functions belonging to different irreps.

Further lowering of the HF energy would thus be only possible by breaking the spin symmetry, leading to a spin-contaminated UHF solution. Since our interest is in pure singlet solutions, we wish to stay within the RHF framework, and do not explore here UHF-type solutions.

### *Immersion of $O^{2-}$ in a Cubic Grid*

We simulate the external potential generated by the MgO crystal by a grid of point charges with alternating signs that are located at the atomic centers in the crystal. Even though this model potential involves only electrostatic interactions, it can provide a useful insight concerning the stabilization of the $O^{2-}$ anion embedded in the crystal. It is important to note here that the inclusion of correlation effects is essential in this case, since the one-electron picture leads to an incorrect description of relative energies of the free (unconfined) neutral atom and its singly charged anion. Indeed, the energy of atomic oxygen at the SCF level with vanishing point charges $|q| = 0$ (i.e., of the free atomic oxygen) is lower than the energy of the $O^-$ anion, implying negative electron affinity, which is obviously incorrect. For this reason we present only CCSD(T) results for the oxygen atom and its singly and doubly charged negative ions.

As can be seen from Fig. 7, the total CCSD(T) energy of the singly charged $O^-$ anion is lower than the energy of the neutral atom, yielding the electron affinity (EA) of 1.4309 eV (in the d-aug-cc-pV5Z basis). This value agrees very well with the experimental EA 1.4611 eV[34]. When $q = 0$, the energy of $O^{2-}$ is higher than the energy of either the oxygen atom or the $O^-$ anion. When we increase the magnitude of point charges forming the grid, the energy of the $O^{2-}$ anion decreases faster than does the energy of $O^-$, while the energy of the neutral oxygen atom remains almost constant with the variation of $|q|$. For $|q| \approx 0.2$, the energy curve for $O^{2-}$ crosses that for the atomic oxygen, and for values of the point charge $|q| \geq 0.75$, the $O^{2-}$ anion becomes more stable than $O^-$. This implies that the extra two electrons are now bound to the oxygen nucleus.

The same trend is reflected in the behaviour of the orbital energies. For $|q| = 0.66$, the orbital energy of the $2p_{x,y,z}$ orbitals becomes negative (–0.0031 a.u.) and further decreases with the increasing charge $|q|$. The dependence of the negative eigenvalues of the Hessian on $|q|$ is similar to that for the confinement due to the spherical, harmonic-oscillator potential ω

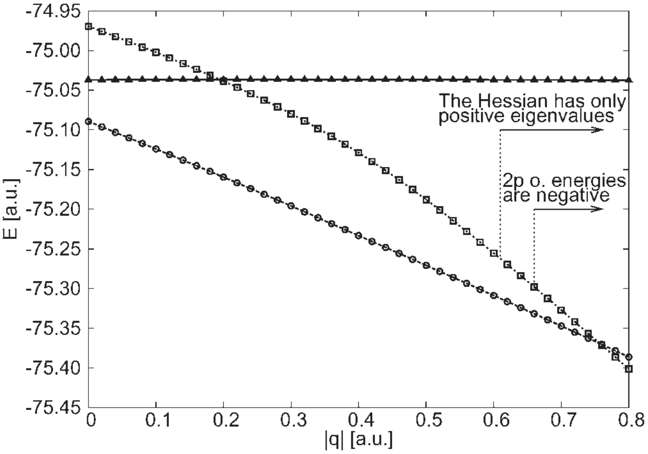

FIG. 7

Total CCSD(T) energy $E$ of the $O^{2-}$ (□), $O^-$ (○), and O (△) systems, immersed in the 5 × 5 × 5 cubic grid of point charges $\pm q$ as a function of the absolute value of the point charge $|q|$, obtained with the d-aug-cc-pV5Z basis set of oxygen. See the text for details shown in Fig. 1. Negative eigenvalues that are associated with a non-degenerate triplet instability appear for $|q|$ lower than 0.60. For point charges larger than 0.60, no BS solutions for $O^{2-}$ can be found.

Besides focusing on the energy of the oxygen atom and its $O^-$ and $O^{2-}$ ions, we have also calculated the dipole polarizabilities $\alpha$ of the $O^{2-}$ anion as a function of $|q|$. With increasing $|q|$ of the point charges forming our grid, and the cell constant defined in Spherical Harmonic-Oscillator-Type Confining Potential, the polarizability $\alpha$ decreases and approaches the value of 46.0 a.u. We note here that the dependence of $\alpha$ on the parameters, and the shape of the cubic grid simulating the crystal structure of MgO were studied earlier by Domene et al.[20]. Our results indicate that the analysis of BS solutions in a general confinement can contribute to our understanding of the behaviour and nature of negatively charged anions in crystals and other environments. A study of polarizabilities of different anions submerged in a point charge grid, as well as in more general confining potentials, will be presented elsewhere.

## CONCLUSIONS

In spite of the fact that in classical electrodynamics a conducting sphere can support an infinitely large electric charge[35], there are severe limitations on charge accumulation in a submicroscopic quantum world. Although most atoms can form stable, singly charged anions, there has been much controversy concerning the existence of long-lived ($>10^{-6}$ s) doubly charged negative ions in the gas phase. In contrast to several claims to the contrary, at least for some heavier atoms[7], there seems to be a unanimous agreement that no such long-lived atomic dianions exist (cf., however, ref.[8] concerning molecular dianions).

Yet, the standard quantum chemical ab initio models, at both HF and correlated levels, yield bona fide solutions for such systems. Trying to obtain such HF solutions via numerical integration approaches[16] leads, however, to the convergence problems[17]. This contrast is not difficult to understand, since the analytical LCAO SCF approaches employ a finite basis set that defines a specific ab initio model and that prevents the electrons from "escaping" from the system. For this reason, the existence of BS solutions for atomic dianions with a lower energy than the ubiquitous SA solution, as is the case for the anions $O^{2-}$ and $S^{2-}$ examined in this paper, is an indication of a tendency of electrons to leave the centrosymmetric structure. Another evidence of this tendency is the fact that in all such BS solutions at least one occupied orbital has a positive energy. Moreover, we observe large changes in both the orbital energies and the roots of the singlet stability problem with the size of the basis set employed, indicating again a tendency of the superfluous electrons to stay as far away from the nucleus as the given model permits. Of course, restricting the trial wave function to a doubly-occupied, closed-shell determinantal form implies that both electrons of a dianion will have a tendency to leave.

These facts can be regarded as an indication that the HF instability and the existence of BS solutions for such systems – which, at least in principle, may be a purely formal indication of the inadequacy of the model employed – points in fact to the process referred to as a spontaneous symmetry breaking. Indeed, examples of both alternatives are known. For example, in the case of the allyl radical, we find doublet instability[28] of the restricted, open-shell HF (ROHF) solutions even when using rather large basis sets[36]. However, in this case the symmetry breaking points out to the inadequacy of the IPM, and a multireference treatment will restore the symmetry. On the other hand, the symmetry breaking in cyclic polyenes $C_nH_n$, which may be regarded as modelling long polyenic chains or polyacetylene, leads to BS charge density wave solutions, which clearly imply the bond-length alternation in real systems (see, e.g., refs[25,37]).

In this paper, we have extended an earlier study of the HF stability of $O^{2-}$ that relied on a Slater-type minimum basis sets to large standard Gaussian-type bases. Moreover, when extending these standard nucleus-centered basis sets with off-center ghost orbitals, in either a symmetric or an asymmetric manner, we find a clear tendency to form BS solutions and the above mentioned tendency to system dissipation. Nonetheless, as pointed out earlier, the doubly negative ions, such as $O^{2-}$, are often postulated – at least formally – in various inorganic complexes and crystals. Clearly, their existence requires a suitable environment that would stabilize such otherwise highly unstable systems.

We have thus examined the stability of HF solutions, as well as the existence of BS solutions, both at the HF and correlated level, in the presence of confining potentials. By relying on either the spherical, harmonic confinement or on the immersion of $O^{2-}$ in a crystal lattice as modelled by a grid of point charges, we find that indeed such electron-rich systems can be stabilized already by a moderately strong confinement. As a test calculation, we have also determined the polarizability of the system in the crystal lattice. It would be certainly of interest to explore in greater detail such properties as the polarizability and hyperpolarizability, as well as other properties of such confined systems, which we hope to pursue in the future.

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## REFERENCES

1. a) Saha B., Mukherjee T. K., Mukherjee P. K., Diercksen G. H. F.: *Theor. Chem. Acc.* **2002**, *108*, 305; b) Sako T., Černušák I., Diercksen G. H. F.: *J. Phys. B* **2004**, *37*, 1091.
2. a) Bielińska-Waz D., Karwowski J., Diercksen G. H. F.: *J. Phys. B* **2001**, *34*, 1987; b) Bielińska-Waz D., Diercksen G. H. F., Klobukowski M.: *Chem. Phys. Lett.* **2001**, *349*, 215; c) Sako T., Diercksen G. H. F.: *J. Phys. B* **2003**, *36*, 1433; d) Sako T., Diercksen G. H. F.: *J. Phys. B* **2003**, *36*, 1681; e) Sako T., Diercksen G. H. F.: *J. Phys.: Condens. Matter* **2003**, *15*, 5487; f) Sako T., Yamamoto S., Diercksen G. H. F.: *J. Phys. B* **2004**, *37*, 1; g) Lo J. M. H., Klobukowski M., Bielińska-Waz D., Diercksen G. H. F., Schreiner E. W. S.: *J. Phys. B* **2005**, *38*, 1143; h) Lo J. M. H., Klobukowski M., Diercksen G. H. F.: *Adv. Quantum Chem.* **2005**, *48*, 59; i) Sako T., Diercksen G. H. F.: *J. Phys.: Condens. Matter* **2005**, *17*, 5159; j) Bielińska-Waz D., Lo J. M. H., Klobukowski M., Schreiner E. W. S., Diercksen G. H. F.: *Chem. Phys. Lett.* **2006**, *422*, 391; k) Lo J. M. H., Klobukowski M., Bielińska-Waz D., Schreiner E. W. S., Diercksen G. H. F.: *J. Phys. B* **2006**, *39*, 2385.
3. a) Sako T., Diercksen G. H. F.: *J. Phys. B* **2003**, *36*, 3743; b) Holka F., Neogrády P., Kellö V., Urban M., Diercksen G. H. F.: *Mol. Phys.* **2005**, *103*, 2747.
4. Sako T., Hervieux P. A., Diercksen G. H. F.: *Phys. Rev. B* **2006**, *74*, 045329.
5. a) Mukherjee P. K., Karwowski J., Diercksen G. H. F.: *Chem. Phys. Lett.* **2002**, *363*, 323; b) Saha B., Mukherjee P. K., Diercksen G. H. F.: *Astron. Astrophys.* **2002**, *396*, 337; c) Okutsu H., Sako T., Yamanouchi K., Diercksen G. H. F.: *J. Phys. B* **2005**, *38*, 917.
6. Paldus J., Čížek J.: *Can. J. Chem.* **1985**, *63*, 1803.
7. a) Stuckey W. K., Kiser R. W.: *Nature* **1966**, *211*, 963; b) Kiser R. W.: *Top. Curr. Chem.* **1979**, *85*, 89.
8. Scheller M. K., Compton R. N., Cederbaum L. S.: *Science* **1995**, *270*, 1160.
9. a) Rohmer M.-M., Bénard M., Blaudeau J.-P., Maestre J.-M., Poblet J.-M.: *Coord. Chem. Rev.* **1998**, *178–180*, 1019; b) Poblet J. M., López X., Bo C.: *Chem. Soc. Rev.* **2003**, *32*, 297.
10. a) Day V. W., Klemperer W. G., Schwartz C.: *J. Am. Chem. Soc.* **1987**, *109*, 6030; b) Bridgeman A. J., Cavigliasso G.: *J. Phys. Chem. A* **2002**, *106*, 6114; c) Mishra A., Abboud K. A., Christou G.: *Inorg. Chem.* **2006**, *45*, 2364.
11. Müller A., Peters F., Pope M. T., Gatteschi D.: *Chem. Rev.* **1998**, *98*, 239.
12. Lindqvist I.: *Acta Crystalogr.* **1952**, *5*, 247.
13. Čížek J., Paldus J.: *J. Chem. Phys.* **1967**, *47*, 3976.
14. Prat R. F.: *Phys. Rev. A* **1972**, *6*, 1735.
15. Hogreve H.: *Phys. Scr.* **1998**, *58*, 25.
16. Froese-Fischer C.: *The Hartree–Fock Method for Atoms: A Numerical Approach*. Wiley, New York 1977.

17. Froese-Fischer C.: Private communication.
18. Spence D., Chupka W. A., Stevens C. M.: *Phys. Rev. A* **1982**, *26*, 654.
19. Chang K. H., McKeown R. D., Milner R. G., Labrenz J.: *Phys. Rev. A* **1987**, *35*, 3949.
20. Domene C., Fowler P. W., Jemmer P., Madden P.: *Chem. Phys. Lett.* **1999**, *299*, 51.
21. a) Kowalski K., Jankowski K.: *Phys. Rev. Lett.* **1998**, *81*, 1195; b) Kowalski K., Jankowski K.: *Chem. Phys. Lett.* **1998**, *290*, 180.
22. Löwdin P.-O.: *Rev. Mod. Phys.* **1963**, *35*, 496.
23. Koutecký J.: *J. Chem. Phys.* **1967**, *46*, 2443.
24. Čížek J., Paldus J.: *J. Chem. Phys.* **1970**, *53*, 821.
25. Paldus J. in: *Self-Consistent Field: Theory and Applications* (R. Carbó and M. Klobukowski, Eds). Elsevier, Amsterdam 1990.
26. Stuber J. L., Paldus J. in: *Fundamental World of Quantum Chemistry* (R. J. Brändas and E. S. Kryachko, Eds), Vol. I. Kluwer, Dordrecht 2003.
27. Thouless D. J.: *The Quantum Mechanics of Many-Body Systems*. Academic Press, New York 1961.
28. a) Paldus J., Čížek J.: *Chem. Phys. Lett.* **1969**, *3*, 1; b) Paldus J., Čížek J.: *J. Chem. Phys.* **1970**, *52*, 2919.
29. Cirula M., Adamowski J., Szafran B., Bednarek S.: *Physica E (Amsterdam)* **2002**, *15*, 261.
30. Varshni Y. P.: *Phys. Status Solidi B* **2001**, *225*, R15.
31. Jaskólski W.: *Phys. Rep.* **1996**, *271*, 1.
32. Andersson K., Barysz M., Bernhardsson A., Blomberg M. R. A., Cooper D. L., Fülscher M. P., de Graaf C., Hess B. A., Karlström G., Lindh R., Malmqvist P.-Å., Nakajima T., Neogrády P., Olsen J., Roos B. O., Schimmelpfennig B., Schütz M., Seijo L., Serrano-Andrés L., Siegbahn P. E. M., Stålring J., Thorsteinsson T., Veryazov V., Widmark P.-O.: *MOLCAS*, Version 5.4. Lund University, Lund 2002.
33. Kendall R. A., Dunning T. H., Harrison R. J.: *J. Chem. Phys.* **1992**, *96*, 6796.
34. Lide D. R. (Ed.): *CRC Handbook of Chemsitry and Physics*. CRC, Boca Raton 1991.
35. Jackson J. D.: *Classical Electrodynamics*. Wiley, New York 1962.
36. a) Paldus J., Čížek J.: *J. Chem. Phys.* **1971**, *54*, 2293; b) Paldus J., Veillard A.: *Chem. Phys. Lett.* **1977**, *50*, 6; c) Paldus J., Veillard A.: *Mol. Phys.* **1978**, *35*, 445.
37. a) Paldus J., Čížek J.: *Phys. Rev. A* **1970**, *2*, 2268; b) Paldus J., Chin E.: *Int. J. Quantum Chem.* **1983**, *24*, 373; c) Takahashi M., Paldus J.: *Int. J. Quantum Chem.* **1985**, *28*, 459; and references therein.