Resonance States of Atomic Di-anions

Thomas Sommerfeld*

Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

(Received 18 February 2000)

Metastable states of O^{2-}, S^{2-}, B^{2-}, and Al^{2-} are studied in the framework of the complex absorbing potential method using highly correlated multireference configuration interaction wave functions. The first row species O^{2-} and B^{2-} are found to be broad resonances showing widths of roughly 1.7 eV, whereas the second row systems S^{2-} and Al^{2-} possess widths clearly smaller than 1 eV. The identified resonance states are compared to the fundamental H^{2-} resonance, and the relationship with recent electron scattering experiments is discussed.

PACS numbers: 32.70.Jz, 32.80.Dz, 34.80.–i

Whereas the nonexistence of *bound* atomic di-anions is now a well established fact [1], only very little is known about metastable or resonance states of doubly charged atomic anions. The simplest system H^{2-} has been studied extensively (see discussion below), but for the heavier atoms one finds only approximate resonance positions that have been obtained from bound state calculations or from an extrapolation of the binding energies of the associated isoelectronic series (see, e.g., Refs. [2–5]). The noteworthy exception is O^{2-} for which an approximate resonance width Γ, which is related to the lifetime $\tau = \hbar/\Gamma$, has been given [3]. Apart from H^{2-} and the estimate for O^{2-}, to our best knowledge, resonance parameters of atomic di-anions have been neither calculated nor measured.

A rough idea of the lifetimes of atomic di-anions can be inferred from the studies on small *molecular* di-anions [1,6,7]. These studies have, however, been concentrated on species observable in mass spectrometers, i.e., with lifetimes $\tau > 10^{-5}$ sec, and investigations on the much shorter lifetimes of electronically unstable systems are rare. So far the only molecular di-anion whose autodetachment lifetime has been studied is ${C_2}^{2-}$ [8,9]. The ${C_2}^{2-}$ closed-shell ${}^1\Sigma_g^+$ state has been found to show a resonance position of 3.5 eV and a width of 0.3 eV. A width of this magnitude is probably at the lower end of what might be expected for atomic systems, but it is certainly reasonable to assume that specific atomic di-anions will possess widths of roughly 1 eV comparable to typical shape-type resonances.

Experimentally atomic di-anions have been addressed by electron-anion scattering, and recently the electron-impact electron-detachment cross section (EIDCS), that is, the cross section associated with the process

$$A^- + e^- \longrightarrow A + e^- + e^- \qquad (1)$$

of three atomic anions $A^- = H^-$, B^-, and O^-, has been investigated using storage ring technologies [10–13]. The observed EIDCS are smooth functions of the impact energy and no hint for a resonant detachment process

$$A^- + e^- \longrightarrow A^{2-} \longrightarrow A + e^- + e^- \qquad (2)$$

via a short-lived di-anion A^{2-} was found. However, on the basis of these observations the existence of resonances cannot be ruled out, since electron scattering from *diatomic* anions suggest the existence of metastable di-anions despite a smooth EIDCS [14]. For example, in electron scattering from ${B_2}^-$ a pronounced structure is detected in the electron-impact dissociation cross section (${B_2}^- + e^- \longrightarrow B^- + B + e^-$), whereas the associated EIDCS exhibits no discernible structure [14,15]. We will come back to the apparent insensitivity of the EIDCS to di-anionic resonances.

The fundamental di-anion H^{2-} is the only atomic di-anion which has so far been studied at high *ab initio* levels of theory. It is now accepted that there are no resonances in electron scattering from the H^- ${}^1S^e$ ground state [5] and the EIDCS has also been found to be smooth [10,12]. The existence of a metastable ${}^4S^o$ state, however, is still disputed. A ${}^4S^o$ $(2p)^3$ resonance state of H^{2-} had been predicted using the complex scaling (CS) method [16–18] in conjunction with a multireference configuration interaction (MR-CI) wave function, and a large width of about 1.7 eV had been found [8,19]. These results were later challenged and claimed to be artifacts, based on two techniques that yield adiabatic curves in the hyper-radius [20,21]. Clearly, artifacts in the earlier calculations can arise only from a too small one- or many-particle basis set, since the CS method itself is beyond any doubt. Already in Refs. [8,19] it had been shown that larger basis sets stabilize the resonance, and the full CI results by Bylicki and Nicolaides [22] confirm convincingly that the ${}^4S^o$ resonance state does indeed exist. The conflict with the findings in Refs. [20,21] thus persists, and we note that the methods used in Refs. [20] and [21] are themselves prone to artifacts, since in Ref. [20] only a dimensionally reduced Schrödinger equation is solved and in Ref. [21] a severely restricted wave function is employed.

It will certainly be difficult to experimentally prove or disprove the existence of the H^{2-} ${}^4S^o$ resonance state, since the resonance is very broad and, more important, the ${}^3P^e$ H^- target state itself is only short-lived. Other atomic

0031-9007/00/85(5)/956(4)$15.00

di-anions should possess smaller widths and more accessible target states, and will therefore be much easier to detect. In this context the following question arises: Which atomic di-anions are the most promising candidates for a long lifetime? One starting point is the electron affinities (EA) of the atoms, since one may expect a di-anion to be relatively "stable," if its isoelectronic anion shows a large electron detachment energy. Let us, however, note that analogies with bound systems can easily lead us astray, since we are looking for small widths which are not necessarily related to low total energies.

Browsing through the periodic table one quickly recognizes that the halogen atoms exhibit by far the largest EAs (see Ref. [23] for EAs of atoms), and thus, one may expect the analogous di-anionic systems O^{2-}, S^{2-}, and the heavier group 16 elements to show relatively long lifetimes. These species possess rare-gas-like closed-shell electronic states, and O^{2-} represents the prototype closed-shell resonance. Both di-anions O^{2-} and S^{2-} are known to exist in the solid state and in solutions, and are—in that context—often viewed as *autonomously stable* ions [6]. This view has been called into question, since it has been known for a long time that O^{2-} and S^{2-} are unstable to electron loss in the gas phase [2,3,24–27]. It is, in particular, problematic to define, e.g., solvent effects, if one cannot refer to the isolated system, because it is unstable in the gas phase. The resonance states investigated in this communication provide a possible reference state for O^{2-} and S^{2-}.

While O^{2-} and S^{2-} are the most obvious candidates for a long lifetime, the next best candidates are not so evident. Based on electron detachment energies of the isoelectronic anions there are essentially three other promising classes. First, the large EAs of the group 16 elements $(\mathrm{O}, \mathrm{S}, \ldots)$ suggest that di-anions of group 15 elements $(\mathrm{N}, \mathrm{P}, \ldots)$ could form long-lived di-anions. However, N^- is unstable with respect to autodetachment and the other group 15 elements possess only tiny first EA. Second, Pt and Au show substantial EAs, and Pt could form a closed-shell di-anion. While the Pt^{2-} system is certainly very interesting, it will be tremendously difficult to obtain even a semiaccurate width, since in addition to the correlation and continuum problems one has to account for relativistic effects. Third, related to the "local" stability of a half-filled p shell, the group 14 elements $(\mathrm{C}, \mathrm{Si}, \ldots)$ possess substantial EAs. Thus, di-anions of group 13 elements $(\mathrm{B}, \mathrm{Al}, \ldots)$ may possess long-lived ${}^4S^o$ states analogous to the H^{2-} ${}^4S^o$ resonance.

In this Letter we investigate closed-shell ${}^1S^e$ resonance states of O^{2-} and S^{2-} as well as ${}^4S^o$ resonance states of B^{2-} and Al^{2-}. To obtain positions and widths we have employed the complex absorbing potential (CAP) method [28] in conjunction with a MR-CI wave function. The CAP/CI method has been described in detail in Refs. [9,29] and provides a simple and efficient method to study resonances using bound state techniques. Let us outline the essential technicalities before we turn to our results.

In the CAP method one computes the Siegert energy

$$E_{\mathrm{res}} = E_r - i\,\frac{\Gamma}{2} \tag{3}$$

of a resonance state, where E_r is the resonance energy and Γ is the associated width. One works with a parametrized non-Hermitian complex-symmetric Hamiltonian operator

$$H^{(\mathrm{CAP})} = H - iW\,, \tag{4}$$

where H is the physical Hamiltonian and W is typically a real potential such as $|\mathbf{r}|^n$. Loosely speaking, a CAP is added to the Hamiltonian to absorb the outgoing electron, and in the complete basis set limit E_{res} does not depend on W. In the framework of a finite basis set E_{res} will, of course, depend on W, and one has to use complex stabilization techniques [28]. Here we have employed two different CAP forms, a spherical quartic CAP as well as a quadratic spherical-box CAP [30], and the error associated with the CAP is small compared with other basis set and correlation effects.

Our underlying one-particle basis set is of triple-ζ quality (see Ref. [31] for B and O and Ref. [32] for Al and S) and has been augmented with two d-type polarization and a $(2s10p)/[2s8p]$ set of diffuse functions (basis I). A more flexible basis set was constructed by decontracting the original valence p-set slightly, adding four d-type and two f-type polarization functions as well as a larger diffuse $(2s13p)/[2s10p]$ set (basis II). In total basis II comprises a $(12s19p4d2f)/[8s15p4d2f]$ set for boron and oxygen and a $(14s22p4d2f)/[8s16p4d2f]$ set for aluminum and sulfur. Molecular orbitals have been obtained from self-consistent field (SCF) calculations using only the compact part of the basis set (for details see Ref. [9]).

The many-particle basis set (configuration space) is then constructed from all single and double excitations with respect to a set of reference configurations. For example, for O^{2-} the reference space contains the $(1s)^2(2s)^2(2p)^6$ closed-shell configuration as well as all singly excited configurations of the type $(1s)^2(2s)^2(2p)^5(np)^1$. In this way the "bound" and the "decaying" aspects of the resonance state are reasonably well balanced [9,29]. The configuration spaces for B^{2-}, Al^{2-}, and S^{2-} are constructed in a similar way and in our present CI calculations only the valence electrons are treated explicitly; i.e., the $1s$ or $1s2s2p$ core electrons, respectively, have been frozen. Moreover, the dimension of the final CI matrix has been reduced via an energy selection scheme [33,34] using thresholds between 0.2 and 0.05 mhartree which led to matrix dimensions between 20 000 and 140 000. The SCF calculations have been performed with the MOLCAS3 package [35], and the CI as well as the CAP matrices have been computed with the multireference CI program developed at the University of Bonn [36]. Selected eigenpairs of the effective Hamiltonian matrix [Eq. (4)] have been computed employing a block Davidson program adapted to the complex symmetric case [37] or the ARPACK library [38].

Let us now turn to our numeric results. The resonance parameters of the investigated species have been collected in Table I. All resonance states are readily identified by their CI vectors and show a pronounced stabilization in the complex stabilization procedure. The closed-shell $^1S^e$ O^{2-} state as well as the $^4S^o$ state of B^{2-} exhibit large widths of roughly 1.7 eV similar to the $^4S^o$ H^{2-} state. This value for the width of O^{2-} is somewhat larger than the extrapolated 1.3 eV of Ref. [3]; however, considering the crude method used in Ref. [3] this is still a remarkable agreement. In going from the first to the second row, for both the group 13 and group 16 elements the resonance widths are considerably reduced to 0.75 and 0.92 eV for S^{2-} and Al^{2-}, respectively. Thus, the lifetime of the investigated species depends essentially on the size of the systems and only weakly on the precise electronic structure. In view of the dominating Coulomb repulsion of the excess electrons, it is not too surprising that the spatially more extended $3p$ shell reduces the effective Coulomb repulsion, and the $(3p)^n$ metastable states of S^{2-} and Al^{2-} live considerably longer than the $(2p)^n$ states of O^{2-} and B^{2-}. It is, nevertheless, remarkable that the widths of the O^{2-} closed-shell state and the fundamentally different B^{2-} and H^{2-} half-filled-shell $^4S^o$ states are so similar.

In this context, electron correlation is of paramount importance, since it has a large influence on the widths as well as on the sizes of the investigated species. Whereas for the three electron system H^{2-} full CI results [22] are available, only restricted configuration spaces are possible for the heavier systems. In contrast to effects of the CAP and the selection procedure, which are small (less than 0.1 eV in the widths) and can be analyzed by comparing different calculations, the missing correlation effects are difficult to estimate. Essentially, there are two sources of error. In the first place, high angular momentum one-particle basis functions are required to accurately describe angular correlation, and, in the second place, there is the effect of triple and higher excitations from the reference space. Core polarization is expected to be only of minor importance in this context. Regarding angular correlation, let us note that upon augmenting the two d-type polarization set of basis I by another d-type and two f-type functions (basis II) we find slightly smaller widths (Table I). Thus, a more flexible one-particle basis set is expected to stabilize the resonance states in the sense that smaller positions and widths are found. This is in-line with a vast body of experience with small anionic systems [7,39] as well as the experience with small di-anions [8,9,22] where many results imply that the missing correlation effects will stabilize the metastable state. Loosely speaking, there is more correlation in an N particle than in an $N - 1$ particle system and more approximate schemes will favor the $N - 1$ particle system. Thus, our widths may be viewed as reasonably accurate "upper bounds" to the true resonance widths. The small differences between the closed-shell and half-filled shell systems may turn out to be more pronounced if higher angular momentum basis function or higher excitations are taken into account, but we have no doubts that the predicted resonances exist and S^{2-} as well as Al^{2-} show indeed widths clearly below 1 eV.

TABLE I. Resonance parameters of the $^1S^e$ states of O^{2-} and S^{2-} and of the $^4S^o$ states of B^{2-} and Al^{2-}. E_r and Γ are given in eV, and the selection threshold T for the CI matrix is 0.1 mhartree.

	Basis I		Basis II	
	E_r	Γ	E_r	Γ
O^{2-}	5.77	1.74	5.65	1.69
S^{2-}	3.90	0.90	3.79	0.75
B^{2-}	3.95	1.75	3.78	1.63
Al^{2-}	3.02	0.95	2.95	0.92

The resonance positions in Table I have been obtained as the difference between the real parts of our Siegert energies and single double CI energies of the respective anion ground states. Our values are considerably lower than the estimates obtained from "bound state" calculations [2,4] or from extrapolation of the binding energy of the associated isoelectronic series [5] with the notable exception of the value for O^{2-} given in Ref. [3]. In particular, the overestimations of the resonance positions in Refs. [2,4] are most probably due to the artificial constrictions imposed to make the system bound.

Let us now briefly discuss the influence of the two-electron detachment channel. This decay process is in principle included in our MR-CI calculations, but the associated neutral decay products are internally not treated at the same high level as the anionic final states. The importance of this decay channel can, however, be estimated from golden rule-like arguments. The golden rule expression for the ratio between the partial widths of the one-electron ($\Gamma^{(1)}$) and two-electron ($\Gamma^{(2)}$) decay channels reads

$$\frac{\Gamma^{(1)}}{\Gamma^{(2)}} = \frac{|\langle d|\hat{H}|f^{(1)}\rangle|^2}{\int dk |\langle d|\hat{H}|f^{(2)}\rangle|^2}, \tag{5}$$

where $|d\rangle$ is the decaying state, $|f^{(1)}\rangle$ and $|f^{(2)}\rangle$ are the respective final states, and the integral in the denominator reflects the fact that in the two-electron decay the energy can be distributed over two electrons. We can estimate the order of magnitude of $\Gamma^{(1)}/\Gamma^{(2)}$ from our CI matrix. For example, for O^{2-} we approximate $|d\rangle$ by the closed-shell configuration $(1s)^2(2s)^2(2p)^6$ and $|f^{(1)}\rangle$ and $|f^{(2)}\rangle$, respectively, by single and double excitations into diffuse orbitals. Taking either the maximum or the average of the corresponding matrix elements we obtain a ratio of roughly 1000. Thus, the contribution of the two-electron detachment channel to the total width is negligible in comparison with our overall accuracy of a few tenths of an eV.

This analysis indicates why the EIDCS is rather insensitive to resonant processes [14]. If in a scattering experiment a di-anionic resonance state is formed, it will most probably decay by the loss of a single electron and only a tiny part will contribute to the EIDCS. Moreover, the resonant part of the cross section will be imposed on a huge background due to the direct EIDCS [40], and thus to detect the resonances one would have to measure the EIDCS very accurately. Alternatively, the scattered electrons could be detected in a crossed beam setup, or the di-anionic resonance state could be observed in process such as

$$A^- + e^- \rightarrow A^{2-} \rightarrow (A^-)^* + e^-, \qquad (6)$$

where an excited state $(A^-)^*$ of the anion A^- is detected [9]. While there are probably no suitable excited states of O^- or S^- in the relevant energy range, there are quintet states of B^- and Al^- [41] that could be populated via process (6).

We have identified resonance states of the four atomic di-anions B^{2-}, O^{2-}, Al^{2-}, and S^{2-}. At the CAP/MR-CI level of theory the first row species B^{2-} and O^{2-} show widths of roughly 1.7 eV similar to the H^{2-} $^4S^o$ state. Despite the expected stabilization of higher correlation effects, we predict these resonances to possess widths clearly larger than 1 eV. The widths of the analogous second row systems are found to be substantially smaller and we predict a width of 0.9 eV for Al^{2-} and a width of 0.75 eV for S^{2-}. The lifetimes of the investigated atomic di-anions seem to depend essentially on system size and surprisingly little on the electronic structure. It remains an open question, if this trend also holds for other species which possess neither closed nor half-filled-shell electron configurations. Moreover, it would be interesting to see if the trend to smaller widths continues in going down groups 13 and 16 (the EAs of the atoms peak in the second row); however, for the heavier elements relativistic effects should be included. We hope this Letter will stimulate the experimental search for these fundamental systems.

I thank Professor L. S. Cederbaum for supporting my work. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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*Thomas.Sommerfeld@urz.uni-heidelberg.de

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