Evidence for a Resonance State of H^{2-}

T. Sommerfeld, U. V. Riss, H.-D. Meyer, and L. S. Cederbaum
Theroretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

(Received 19 March 1996)

A resonance state with three equivalent electrons and one proton has been identified. Large scale calculations have been performed in the framework of the complex-rotated Hamiltonian and indicate strong correlation effects in this system. The findings are rationalized by comparing with bound doubly charged anions and calculations in the infinite dimension limit. [S0031-9007(96)00636-9]

PACS numbers: 31.25.–v, 32.70.Fw, 32.80.Dz

Singly charged negative ions in the gas phase have attracted considerable attention over the past decades, whereas the existence of free doubly charged negative ions has remained a curiosity and only recent experimental and theoretical studies have definitely shown that small dianions may exist as isolated entities [1]. Surprisingly, many dianions which are well known in solids or solutions cannot permanently bind two extra electrons in the gas phase, and, in contrast, many systems which are found or predicted to form stable free doubly charged anions are not known in classical chemistry. In view of the Coulomb repulsion between the two extra electrons the question "Which is the smallest molecular or atomic system that can bind two additional electrons?" has drawn substantial interest. Out of the many findings that have been recently reviewed [1,2], let us briefly mention two outstanding examples. Doubly charged carbon clusters $C_n{}^{2-}$ ($n = 7$–28) with lifetimes $>10^{-6}$ s have been observed in a mass spectrometer [3] and dianions of the type $MX_3{}^{2-}$ ($M =$ Li, Na, K; $X =$ F, Cl) have been predicted theoretically to form stable dianions [4].

The simplest doubly charged negative ion is H^{2-}. This system has been a matter of controversial debate in the literature, and here we briefly outline its "history." The H^{2-} ion possesses no bound electronic state, i.e., no state which is stable with respect to electron autodetachment. On the one hand, it has been proved that one proton cannot permanently bind three electrons [5], which is a special case of Lieb's more general theorem [6], and on the other hand, high quality *ab initio* calculations [7,8] have shown that H^{2-} has no excited bound state, i.e., states which are bound with respect to the correspondingly excited H^- ion and a free electron. These findings restrict potentially long lived H^{2-} states to shape or core-excited shape resonances (using the notion of [9]). Moreover, the observation of a pronounced structure in the $e + H^- \rightarrow H + 2e$ collision process has been interpreted as the formation of two metastable states of H^{2-} [10–12]. Stabilization calculations which determined two ${}^2P^o$ resonances at roughly the energies observed supported the experimental findings [13,14]. Twenty years later, however, these interpretations have been questioned, and it was claimed that the observed resonance phenomena could not correspond to H^{2-} [15]. Among the arguments presented are calculations which show that the theoretical results in Refs. [13] and [14] are most probably artifacts of a too small basis set. Furthermore, the resonance structures had been detected at energies slightly above the threshold for complete breakup of the system into a proton and three free electrons, which contradicts Simon's theorem [15,16]. (Simon showed that, in any many-particle system experiencing only Coulombic forces, resonances cannot exist above the threshold for complete disintegration of the system.) The authors conclude that there are no H^{2-} resonances above the triple-escape threshold, and, thus, there are no indications whatsoever for a long lived state of H^{2-} in the literature.

Nevertheless, from our experience with bound dianions, we would expect a H^{2-} state with three equivalent electrons to be a promising candidate for a "long" lifetime. This criterion is fulfilled for the $(2p^3)^4S^o$ state, which has been found to be unbound as mentioned above [7,8]. But, the same state is bound for He^- [8], i.e., He^- $(2p^3)^4S^o$ is bound with respect to He $(2p^2)^3P^e$. We thus decided to study the ${}^4S^o$ state, treating the nuclear charge Z as a parameter. Starting from $Z = 2$ (He, bound) we reduced Z and followed the ${}^4S^o$ state as it became unbound and moved into the $(2p^2\epsilon p)$ continuum. In the following, we describe briefly the theoretical techniques employed to calculate the resonance parameters for different Z values. We then discuss our results and draw connections with isoelectronic species as well as related dianionic systems to elucidate the nature of the metastable H^{2-} ion.

In this study the complex-rotation (CR) method [17–21] has been used to describe the resonance state theoretically. In this method the electronic coordinates $\{r\}$ of the Hamiltonian are rotated into the complex plane, that is, $H(\{r\}) \rightarrow H(\{e^{i\theta}r\}) \equiv H(\theta)$. If the rotation angle θ is large enough, the wave function of the resonance state vanishes as any of the electronic coordinates tends to infinity, and, thus, the wave functions of both the bound and resonance states are represented by square integrable functions and can be expanded in a standard L^2 basis. The resonance parameters can then be obtained by solving a complex symmetric eigenvalue problem, where the complex energy $E_{\mathrm{res}} = E - i\Gamma/2$ gives the resonance position E and lifetime $1/\Gamma$. In practical calculations it has been observed that the resonance eigenvalue rotates toward the resonance position, slows down, and then rapidly rotates away when θ is increased; i.e., there is a θ_{opt} for which the finite basis set describes the resonance state in an optimal way, and the best value for the resonance energy is found by inspecting the complex spectrum of the Hamiltonian matrices $H(\theta)$ at various angles.

Since, in the H^{2-} system, the nuclear potential "felt" by the electrons is weaker than the interelectronic repulsion, electron correlation may be expected to be extremely important. Thus, we employed the multireference configuration interaction (MRCI) approach to construct the three-particle basis functions for the complex-rotated Hamiltonian. The underlying one-particle basis sets consist of uncontracted Cartesian Gauss type orbitals (GTO), and in this Letter we present data for basis sets comprising $18p$ and $7s18p5d$ functions, respectively. Furthermore, the effects of one or two additional *f*-type functions are examined for $Z = 1$. The configuration space was then generated by all single and double excitations relative to a set of 18 (np^3)-type reference configurations. By this means, a full-CI (FCI) expansion within the *p* orbital space is obtained, and all excitations of one or two electrons into the *s*, *d*, or *f* orbitals are taken into account. The real and imaginary parts of the so-defined Hamilton matrix were computed using the MOLCAS package of programs [22] in conjunction with the MRCI program of Engels, Pless, and Suter [23]. Subsequently, a band Lanczos algorithm [24] adapted to the case of complex symmetric matrices was employed to calculate the complex spectrum. The trajectory of the resonance in the complex energy plane shows a pronounced stability with respect to θ once the resonance is uncovered (see Fig. 1). There, its velocity $|dE/d\theta|$ is smaller by at least 2 orders of magnitude than that of all the other trajectories. Within the basis sets studied, the existence of the resonance state is beyond doubt. Further details regarding the basis sets and the computational procedure will be described in a forthcoming publication.

We now turn to the discussion of our numerical results. To give an impression of the energy changes involved in going from $Z = 2$ to $Z = 1$, we have plotted the total energies of three states which are essential in the present context (see Fig. 2). The continuous and dashed curves show the energy for the $(2p^1)^2P^o$ and $(2p^2)^3P^e$ states, respectively. The energy of the former state simply equals $-Z^2/8$, whereas the data for the latter state have been computed at the FCI level of theory employing the $18p$ basis. Clearly, the two-electron $^3P^e$ state is bound for $Z = 2$, but in going to smaller nuclear charges the $(2p^2)$ and $(2p^1)$ energies approach each other, and for $Z = 1$ the two states have virtually the same energy. In fact, the $(2p^2)^3P^e$ state of H^- is bound by only about 0.00035 a.u. [25]. For comparison, the real part of the complex energy of the investigated three-electron $(2p^3)^4S^o$ state obtained at the FCI/$18p$ level of theory is also shown in Fig. 2 (dotted curve). As mentioned above, this state is bound with respect to electron loss for $Z = 2$; however, if Z is decreased it becomes rapidly unbound and moves into the $(2p^2\epsilon p)$ continuum. Decreasing Z further, the $(2p^3)^4S^o$ state becomes unbound even with respect to the $(2p^1)^2P^o$ state at Z slightly below 1.4, i.e., the channel to the $(2p^1\epsilon p\epsilon' p)$ continuum opens. Despite that, at $Z = 1$, the energy of the $(2p^3)^4S^o$ state is still clearly negative (-0.063 a.u.), i.e., below the threshold of the complete breakup of the system, and thus Simon's theorem is not violated. We note that the real part of the energy of the $^4S^o$ state is decreased to -0.071 and

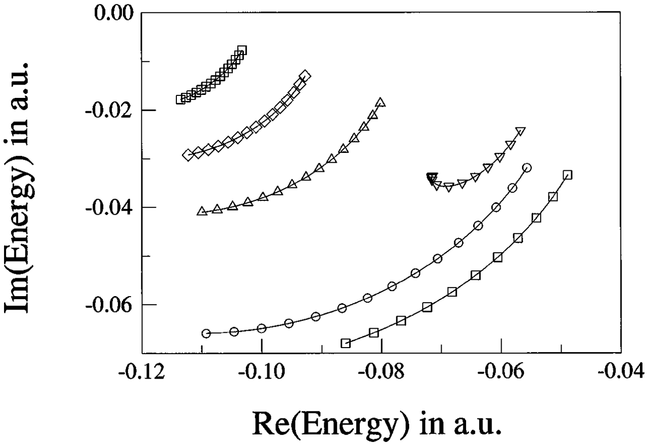

FIG. 1. The eigenvalue trajectories of the resonance and five typical other states in the complex energy plane for rotation angles $14° \leq \theta \leq 42°$ in steps of 2°. The $7s18p5d$ basis set has been used.

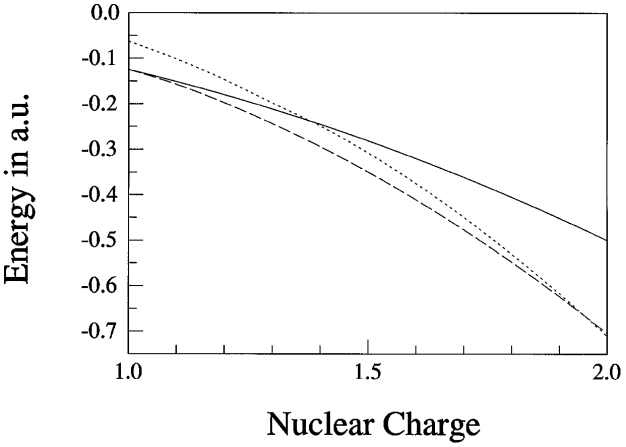

FIG. 2. Total energy of three different electronic states discussed in the text. Continuous line, one-electron $(2p^1)^2P^o$ state; dashed line, two-electron $(2p^2)^3P^e$ state; dotted line, three-electron $(2p^3)^4S^o$ state. For the latter state, the real part of the complex energy is shown.

-0.072 a.u., if *d*- and *f*-type functions are added to the basis set, respectively.

Let us now examine the corresponding lifetimes of the $(2p^3)^4S^o$ state. Our results obtained with different basis sets are displayed in Fig. 3. Two trends catch the eye immediately. First, the lifetime does not decrease in a smooth way with decreasing *Z*, the curves exhibit a "cusp" around $Z = 1.3$. We attribute this effect to the opening of the $(2p^1\epsilon p\epsilon' p)$ two-particle breakup channel. Second, for any particular *Z* value the lifetime increases as the basis set is enlarged; e.g., for $Z = 1$, the imaginary part of the energy of the resonance state is increased from -0.043 a.u. for the $18p$ basis set to -0.034 a.u. when *s*- and *d*-type functions are added, and to -0.032 a.u. if additional *f*-type functions are included. Thus, in going to larger basis sets, the resonance state is stabilized in two respects: its energy is decreased and its lifetimes is increased. Furthermore, for the $7s18p5d$ basis set, the cusp in the lifetime curve is shifted to smaller *Z* values. This indicates a later crossing with the $(2p^1)^2P^o$ state, and thus also reflects the stabilization of the $^4S^o$ resonance state. These tendencies further exclude the possibility that our findings are numerical artifacts due to basis set limitations. Let us note that the particular values for the lifetime depend only weakly on the respective number of additional *d*- or *f*-type functions (i.e., one function suffices as long as the corresponding exponent has an appropriate value), in contrast to the behavior of the complex energy as a function of the rotation angle θ. Here, only if sufficiently many basis functions of a given angular momentum are included is the basis set able to approximate the wave function over an appreciable θ range, and consequently yields a greater stability of the complex eigenvalue with respect to θ. As our final result, we predict a long lived H^{2-} state at an energy of about 1.4 eV above the $(2p^2)^3P^e$ state of H^- with a lifetime of about $\hbar/1.7$ eV $= 3.8 \times 10^{-16}$ s. We hope that these results will stimulate the search for the H^{2-} resonance. It is pointed out that this state would not be seen in electron scattering from the H^- ground state. We propose instead to scatter from the $(2p^2)^3P^e$ state, a challenging experiment indeed.

How can the existence of a long lived H^{2-} state be rationalized? Consider for comparison the $LiF_3{}^{2-}$ dianion [4], which may be thought of as three F^- anions bound to a Li^+ cation resembling in this way three "heavy" electrons and one proton. $LiF_3{}^{2-}$ is stable with respect to electron autodetachment and metastable with respect to F^- loss, thus representing a very long lived resonance of the corresponding four-particle system. The reason for its stability is the triangular geometrical configuration (D_{3h} symmetry) which allows the Coulomb attraction between the central Li^+ cation and the three F^- ligands to overcompensate the Coulomb repulsion in the system. An analogous effect may stabilize H^{2-}, if the electronic motion is correlated in such a way as to maintain an approximately triangular configuration around the nucleus. There is some evidence for such a correlation in the literature. Nicolaides *et al.* calculated the expectation value for the angle between two electrons with respect to the nucleus for several bound $(np^3)^4S^o$ states of Li [26,27]. For $n = 2$, an angle of 90° is obtained which might be expected for a (p^3) electron configuration. For larger *n* values, however, the angle increases and tends to a limit of 120°. Thus, the more extended the system becomes, the closer a situation analogous to $LiF_3{}^{2-}$ is approached. The same tendency is observed when studying the system in the large dimension limit. Instead of solving the Schrödinger equation in the real three-dimensional space, one solves it in the infinite-dimensional space and extrapolates the results to the real space by a suitable expansion [28,29]. In general, the solution in the large dimension limit is much simpler to obtain, and the results qualitatively reflect those of the original Schrödinger equation [30]. In this limit, in which

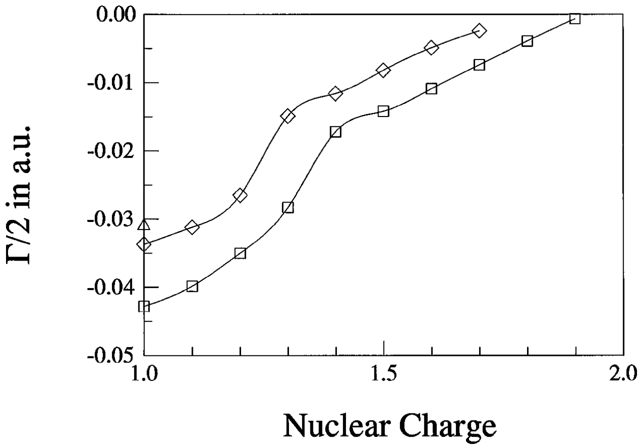

FIG. 3. The imaginary part of the complex energy of the $(2p^3)^4S^o$ state is shown. The curves give the results for different basis sets. Squares, $18p$ basis; diamonds, $7s18p5d$ basis; triangle, $7s18p5d2f$ basis.

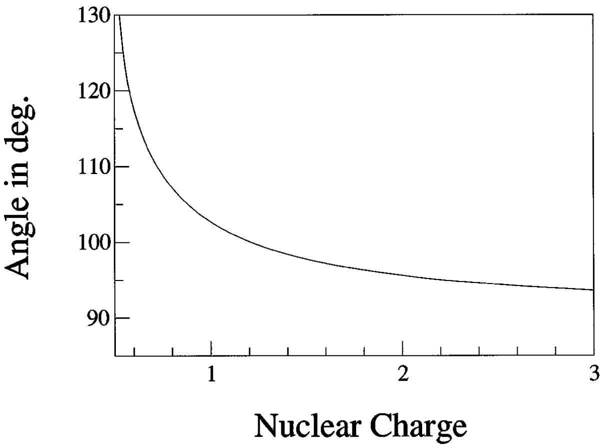

FIG. 4. Angle between two electrons with respect to the nucleus of a three-electron atom in the large dimension limit.

the electrons are localized in space and equivalent, the angle γ of the electrons with respect to one another can be obtained analytically [31]. For a three-electron system the value of γ in dependence of the nuclear charge is shown in Fig. 4. Obviously, the trend is the same as before. When Z is decreased, the system becomes more extended and γ becomes larger. In light of these findings, the lifetime increase which occurs in our calculations in going from the $18p$ to the $7s18p5d$ basis set may be understood in the following terms. Employing a basis set comprising only a p-type function, we enforce an average angle of 90° between the electrons. In contrast, by taking excitations into s- and d-type orbitals into account, we allow for a larger average angle and by this means the H^{2-} system is stabilized.

This work would not have been possible without the help of Bernd Engels and Hans Ulrich Suter who generously put the new version of the MRCDI program at our disposal, answered our questions, and helped us change their code. Computer time has been provided by the Rechenzentrum der Universität Heidelberg. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

[1] M.K. Scheller, R.N. Compton, and L.S. Cederbaum, Science **270**, 1160 (1995), and references therein.
[2] R.N. Compton "Negative Ions (Multiply Charged Negative Ions)" edited by V. Esaulov (Cambridge University Press, Cambridge, England, to be published).
[3] S.N. Schauer, P. Williams, and R.N. Compton, Phys. Rev. Lett. **65**, 625 (1990).
[4] M.K. Scheller and L.S. Cederbaum, J. Chem. Phys. **99**, 441 (1993).
[5] J.M. Levy-Leblond, J. Phys. B **4**, L23 (1971).
[6] E.H. Lieb, Phys. Rev. Lett. **52**, 315 (1984).
[7] C.F. Bunge and A.V. Bunge, Int. J. Quantum Chem. **12**, 345 (1978).
[8] D.R. Beck and C.A. Nicolaides, Chem. Phys. Lett. **59**, 525 (1978).
[9] J. Simons and K.D. Jordan, Chem. Rev. **87**, 535 (1987).
[10] D.S. Walton, B. Peart, and K. Dolder, J. Phys. B **3**, L148 (1970).
[11] D.S. Walton, B. Peart, and K. Dolder, J. Phys. B **4**, 1343 (1971).
[12] B. Peart and K. Dolder, J. Phys. B **6**, 1497 (1973).
[13] H.S. Taylor and L.D. Thomas, Phys. Rev. Lett. **28**, 1091 (1972).
[14] L.D. Thomas, J. Phys. B **7**, L97 (1974).
[15] F. Robicheaux, R.P. Wood, and C.H. Greene, Phys. Rev. A **49**, 1866 (1994).
[16] B. Simon, Int. J. Quantum Chem. **14**, 529 (1978).
[17] E. Balslev and J.M. Combes, Commun. Math. Phys. **22**, 28 (1971).
[18] B. Simon, Commun. Math. Phys. **27**, 1 (1972).
[19] B. Simon, Ann. Math. **97**, 247 (1973).
[20] W.P. Reinhardt, Annu. Rev. Phys. Chem. **33**, 207 (1982).
[21] B.R. Junker, Adv. At. Mol. Phys. **18**, 207 (1982).
[22] K. Andersson, M.R.A. Blomberg, M.P. Fülscher, V. Kellö, R. Lindh, P.-A. Malmqvist, J. Noga, J. Olsen, B.O. Roos, A.J. Sadlej, P.E.M. Siegbahn, M. Urban, and P.O. Widmark, MOLCAS Version 3, University of Lund, Sweden, 1994.
[23] B. Engels, H.U. Suter, V. Pless, R.J. Buenker, and S.D. Peyerimhoff (private communication).
[24] H.-D. Meyer and S. Pal, J. Chem. Phys. **91**, 6195 (1989).
[25] G.W.F. Drake, Phys. Rev. Lett. **24**, 126 (1970).
[26] C.A. Nicolaides, M. Chrysos, and Y. Komninos, Phys. Rev. A **41**, 5244 (1990).
[27] Y. Komninos, M. Chrysos, and C.A. Nicolaides, Phys. Rev. A **38**, 3182 (1988).
[28] L.G. Yaffe, Rev. Mod. Phys. **54**, 407 (1982).
[29] E. Witten, Phys. Today **33**, 38 (1980).
[30] L.G. Yaffe, Phys. Today **36**, 50 (1983).
[31] J.G. Loeser, J. Chem. Phys. **86**, 5635 (1987).