Nonexistence of Resonances in H^{2-}

Toru Morishita and C. D. Lin
Department of Physics, Cardwell Hall, Kansas State University, Manhattan, Kansas 66506

C. G. Bao
Department of Physics, Zhong-Shan University, Guangzhou, People's Republic of China

(Received 15 August 1997)

The controversy of the existence of resonances in H^{2-} ions is revisited. We calculate the hyperspherical adiabatic potential curves for H^{2-}. For $^4S^0$ symmetry all the potential curves are repulsive, and thus no bound or resonance states exist. This conclusion contradicts the recent calculations of Sommerfeld *et al.* [Phys. Rev. Lett. **77**, 470 (1996); Phys. Rev. A **55**, 1903 (1997)], where a $^4S^0$ resonance has been predicted. We also calculate the potential curves for several values of the nuclear charge Z ranging between 1 and 2 and show that no resonance or bound state can exist for Z less than about 1.6. Based on the general ordering of energies of intrashell states, we show the conclusion of Sommerfeld *et al.* is in contradiction with experiment. [S0031-9007(97)05022-9]

PACS numbers: 31.15.Ja, 31.25.Jf

Singly charged atomic negative ions are known to exist and have been widely studied. Since the early days, both physicists and chemists have been fascinated with the possibility of finding bound or resonant states of doubly charged atomic negative ions. In particular, the simplest dianion, H^{2-}, has attracted a great deal of interest. First experiments [1,2] in the 1970s in merged beam collisions between electrons and H^- ions observed two broad features at energies above the full breakup ($e^- + H^- \rightarrow e^- + e^- + e^- + p$) threshold. These features were immediately "confirmed" by calculations based on the stablization method [3], and the structures were attributed to the two $^2P^0$ resonances with approximate $2s^22p$ and $2p^3$ configurations. However, the interpretation and the agreement with experiment is not convincing. These "resonances" lie above the complete breakup threshold and therefore contradict the general Simon's theorem [4], which states that no resonances can exist above the full disintegration limit if the constituents interact only via Coulomb forces.

The existence of $^2P^0$ resonances has been questioned since 1977 [5,6] and later again in 1994 using an extensive R-matrix calculation [7]. These results showed no evidence of any $^2P^0$ resonances. Modern merged-beam collision experiments are carried out using cooled ions from a storage ring. Andersen *et al.* [8] performed $e^- + D^-$ collisions using the Aarhus storage ring and they found no evidence of resonances anywhere for electron energy between 2 and 30 eV with respect to the ground state of the D^- ion. A similar experiment for H^- was carried out using Tokyo's ion storage ring and again no resonances were observed [9]. Thus after about 25 years, it seems that both experiments and theories agree that there are no resonance states in H^{2-}.

The issue of resonances in H^{2-}, however, is far from over. In two recent papers [10,11] Sommerfeld *et al.* performed large-scale calculations on the $^4S^0$ state of H^{2-}. They found a resonance with the approximate $2p^3$ configuration; it has an energy of 1.4 eV above the $2p^2\,{}^3P^e$ threshold of H^- and a width of 1.7 eV. The existence of such a broad resonance is indeed very uncommon. It spans over several inelastic thresholds of H^-. Since the predicted resonance is a $^4S^0$ state, it does not contradict with existing experimental results, as merged-beam experiments can populate only doublet states. It is the aim of this Letter, however, to provide counterevidences to dispute their claim.

In our approach, we solved the three-electron atom in hyperspherical coordinates within the adiabatic approximation using the hyperradius as an adiabatic parameter. To first order we obtained a family of adiabatic potential curves which in turn provide an estimate of the positions of all the resonances. This approach has been applied successfully previously in the study of both the shape and Feshbach resonances of H^- [12], the bound states of He trimers [13], and other three-body systems [14].

The hyperspherical approach for three-electron systems has been applied to a previous investigation [15] for the $^2P^0$ symmetry of H^{2-}. The hyperspherical potential curves were found to be all repulsive and thus it was concluded that there is no possibility of any resonances, in agreement with other theoretical and experimental conclusions. In lieu of the prediction of Sommerfeld *et al.* we calculate the potential curves for the $^4S^0$ symmetry of H^{2-}. We found that all the potential curves are repulsive which cannot support any bound states or resonances.

In hyperspherical coordinates for three-electron atoms, the radial distances r_1, r_2, and r_3 of the three electrons from the nucleus are replaced by a hyperradius R and two hyperangles α_1 and α_2, defined by

$$\begin{aligned} r_1 &= R \sin\alpha_2 \cos\alpha_1 \,, \\ r_2 &= R \sin\alpha_2 \sin\alpha_1 \,, \qquad (1) \\ r_3 &= R \cos\alpha_2 \,. \end{aligned}$$

Together with the spherical angles $\hat{r}_i$ $(i = 1, 2, 3)$ for each electron, the nine spatial hyperspherical coordinates for the three-electron atoms are $(R, \alpha_1, \alpha_2, \hat{r}_1, \hat{r}_2, \hat{r}_3)$. We shall use $\Omega = \{\alpha_1, \alpha_2, \hat{r}_1, \hat{r}_2, \hat{r}_3\}$ to denote all the angles collectively. The Schrödinger equation for the rescaled wave function $\psi = R r_1 r_2 r_3 \Psi$ then reads

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial R^2} + H_{\mathrm{ad}}(\Omega; R) - E\right]\psi = 0\,, \qquad (2)$$

where the adiabatic Hamiltonian $H_{\mathrm{ad}}(\Omega; R)$ is an operator in the hyperangles Ω and depends parametrically on R. The total wave function is written as

$$\psi^S = \sum_\nu F_\nu^S(R)\left(\sum_{S_{12}} \Phi_\nu^{S,S_{12}}(\Omega; R)\chi_{S_{12}}^S\right), \qquad (3)$$

where the total spin S has been written explicitly. In this equation $F_\nu^S(R)$ is the radial function, $\Phi_\nu^{S,S_{12}}$ is the spatial part of the adiabatic channel function, and $\chi_{S_{12}}^S = [\{\chi(1)\chi(2)\}^{S_{12}}\chi(3)]^S$ is the total spin function. The function $\Phi_\nu^{S,S_{12}}$ and its associated potential energy $U_\nu^{S,S_{12}}(R)$ are defined as solutions of the hyperspherical adiabatic eigenvalue problem

$$[H_{\mathrm{ad}}(\Omega; R) - U_\nu(R)]\Phi_\nu(\Omega; R) = 0\,. \qquad (4)$$

All the functions $\Phi_\nu^{S,S_{12}}$ which are solutions of (4) are required to satisfy the Pauli exclusion principle; i.e., the function in (3) should be totally antisymmetric.

In order to construct channel functions satisfying appropriate symmetries, we adopt a two-step numerical procedure. In the first step we include only electron-nucleus interaction to obtain basis functions which satisfy the symmetry constraints. In the second step the electron-electron interaction is diagonalized, giving the adiabatic potential curves.

We use the numerical procedure outlined above to study the ${}^4S^0$ states in H^{2-} where a very broad resonance has been predicted by Sommerfeld *et al.* In the following we will use the adiabatic hyperspherical potential curves in *three* different ways to draw the conclusion that there are no bound or resonance states.

(1) The adiabatic hyperspherical potential curves.—In Fig. 1 we show the first few ${}^4S^0$ hyperspherical potential curves for H^{2-}. The energy E_r and width Γ_r of the resonance obtained by Sommerfeld *et al.*, as well as the asymptotic energies of H$(n = 2, 3, 4)$ limits are also indicated. To begin with, all the potential curves are repulsive. They do not have the attractive wells that are needed in order to support bound states or resonances.

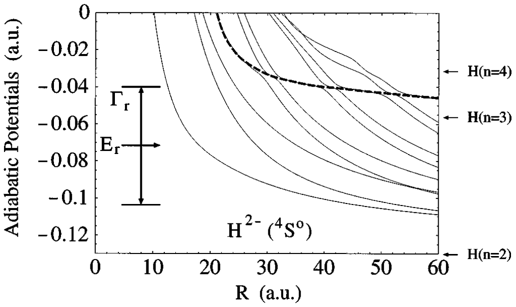

FIG. 1. The first few hyperspherical potential curves for ${}^4S^0$ states of H^{2-}. Also indicated are the energies of H$(n = 2, 3, 4)$ thresholds. The $2p^2\,{}^3P^e$ state of H^- is 7.5 mRy below the H$(n = 2)$ threshold. The energy and the width of the resonance predicted by Sommerfeld *et al.* [10,11] are also indicated.

The potential curves are calculated with the trios of orbital angular momentum quantum numbers $(\ell_1, \ell_2, \ell_3) = (1, 1, 1)$ and $(1, 2, 2)$. Combinations of other higher angular momenta have been included but they have little effect on the calculated curves. At large R, where one or two electrons are far from the nucleus, the system breaks up into $H^- + e^-$ or $H + e^- + e^-$. The lowest curve approaches the $2p^2\,{}^3P^e$ state of H^- which lies at an energy of 7.5 mRy below the H$(n = 2)$ threshold [16,17]. Note that the lowest potential curve is fully repulsive. If there is a $2p^3$ bound state associated with this curve, then a potential well is expected and the energy will be below the $2p^2\,{}^3P^e$ state of H^-. If there is a shape resonance, then there should be a potential well at small R together with a potential barrier at large R where the barrier should be higher than the calculated resonance energy (marked by E_r in the figure). There are no such potential wells or potential barriers in the curves of Fig. 1.

In Fig. 1 we also show a few higher potential curves. Since there are no other bound states (or doubly excited states) of H^- of the correct symmetry that can be formed in the energy region near the H$(n = 2)$ limit, all of the other potential curves shown as solid lines are expected to converge to the H$(2p)$ limit for $R \to \infty$. They represent the discretization of the H$(2p) + e^- + e^-$ continuum states in the finite region of R. Since the potential curves are calculated only up to $R = 60$, there are only a finite number of such curves in the range of energy shown.

In Fig. 1 we also show a dashed curve which is obtained by treating the adiabatic avoided crossings diabatically. This curve is expected to approach the $3p^2\,{}^3P^e$ state of H^- at large R. It is repulsive and thus no bound states or resonances are expected.

We comment that the hyperspherical approach is very suitable for studying shape resonances. The well-known ${}^1P^0$ shape resonance above the H$(n = 2)$ limit in H^- is well represented by a potential curve which has an attractive well at small R and a potential barrier at large R [12]. Similarly, other known shape resonances in H^- near the H$(n = 3)$ threshold are also well represented by such potentials [18]. A shape resonance in positronium negative ion Ps^- is also represented by a hyperspherical potential which has the expected shape [14]. In other words, the known shape resonances for the three-body systems can all be represented by hyperspherical adiabatic potential curves which have attractive wells at small R and repulsive barriers at large R. This in fact is the strength of the hyperspherical method since the potential curve provides a good estimate of whether bound states (or resonances) can exist or not without directly calculating the energy levels.

The discussion above does not include the effect of coupling among the potential curves. However, the effect of the coupling can be estimated from the magnitude of the diagonal second-order coupling term, $-\langle\Phi_\mu|(\partial^2/\partial R^2)|\Phi_\mu\rangle$. This term is positive definite and adds to the potential $U_\mu(R)$. We have calculated this term for the lowest curve and found that it is small at all R and thus the conclusion above is not changed.

(2) The Z dependence of the $^4S^0$ potential curves from $Z = 1$ to $Z = 2$. An alternative assessment of the prediction of the resonance in H^{2-} is to examine the evolution of the hyperspherical potential curves as the nuclear charge Z decreases from $Z = 2$ to $Z = 1$ for the three-electron systems. For this purpose we show the lowest $^4S^0$ potential curve for $Z = 2$, 1.8, 1.6, 1.4, 1.2, and 1 in Fig. 2. For easier comparison, we normalize all the calculated potential curves at $ZR = 60$ to -1.0. Thus the relative depth of the potential wells, if they exist, can be compared directly. For $Z = 2$, the He^- is known to have one bound state for this symmetry. The accurate energy level calculated by [19] is $-0.722\,952$ a.u. From the present potential curve for $Z = 2$, the lowest energy calculated with (without) the second-order diagonal term is -0.7201 a.u. (-0.7299 a.u.). Within the one-channel approximation, these two energies provide the upper and lower bounds to the exact solution [20]. Clearly our calculated energy level including the second-order diagonal term is very close to the result of [19]. This illustrates that the adiabatic approximation is quite adequate for obtaining reliable binding energy for the lowest $2p^3\,{}^4S^0$ state of He^-. We thus expect the adiabatic approximation to work well also for H^{2-}. In fact adiabaticity is an even more reliable assumption for H^{2-} since it is a more diffuse system. In studying two-electron atoms the adiabatic approximation in general works better for H^- than for He [17,21].

From the potential curves shown in Fig. 2 it is clear that for $Z = 1.8$ there is still a weak attractive well. For $Z = 1.6$ the potential well is too shallow to support any bound state. We estimate that to have a bound state the charge has to be greater than 1.6 approximately. (No attempt was made to determine the precise value of Z where a near-zero energy bound state begins to disappear.)

Based on the potential curves in Fig. 2 we can also conclude that there is no $^4S^0$ bound state or resonance associated with H^{2-}.

(3) Relative energies of intrashell triply excited states in three-electron systems. A further argument against the claim of a $^4S^0$ resonance in H^{2-} is to examine the relative energies of intrashell states of a three-electron or three-valence electron system. In a recent paper, Bao *et al.* [22] analyzed the nodal surfaces of the angular part of wave functions resulting from constraints imposed by the quantum symmetry—i.e., the total orbital and spin angular momenta, the parity, and the Pauli exclusion principle. It was concluded that among the instrashell states, the $^2P^0$ state should have the lowest energy, followed by the $^4P^e$ state. These two states have no nodal surfaces in their wave functions in the body frame, while all the other states, including the $^4S^0$ states, have nodal surfaces in at least one of the internal coordinates. This implies that the energy of the $^2P^0$ state should always be lower than that for the $^4S^0$ state for any systems. This ordering is in fact the case for Li and He^-, as well as for other three-valence electron systems. In Fig. 3 we show the lowest potential curves for the $^2P^0$, $^4P^e$, and $^4S^0$ symmetries of H^{2-}. Obviously the $^4S^0$ curve is much higher than the other two curves, in agreement with the general consideration discussed above.

Following this general argument, if a $^4S^0$ resonance indeed exists as claimed by Sommerfeld *et al.*, then a Feshbach or shape resonance should exist for the $^2P^0$

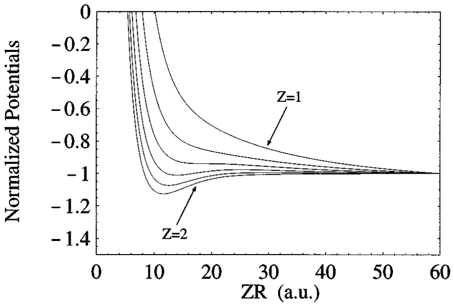

FIG. 2. The lowest $^4S^0$ potential curve for a three-electron system with "nuclear charge" Z ranging from 2 (for He^-) to 1 (for He^{2-}) in steps of 0.2 showing the gradual disappearance of the attractive potential well as Z decreases.

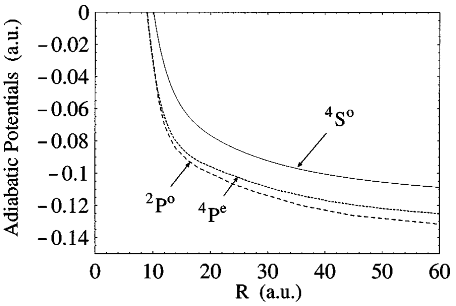

FIG. 3. The lowest potential curves for $^2P^0$, $^4P^e$, and $^4S^0$ symmetries for H^{2-}. If triply excited states exist for H^{2-}, they are expected to be bound by these potential curves. Note that $^4S^0$ is expected to be more repulsive than the other two symmetries (see text).

symmetry at a lower energy. However, such a $^2P^0$ resonance has not been seen in recent experiments [8,9], nor in other calculations [7,15]. Thus the prediction of a $^4S^0$ resonance can be ruled out based on this general argument and known theoretical and experimental results.

In summary we reexamined the new predictions of the existence of a $^4S^0$ resonance in H^{2-} as suggested by the recent calculations of Sommerfeld *et al.* [10,11]. From the calculated $^4S^0$ hyperspherical potential curves, from the dependence of these curves with the nuclear charges between $Z = 2$ and $Z = 1$, and from the general relative energies among instrashell states of different symmetries, we concluded that there exists no $^4S^0$ resonances in H^{2-}, in contradiction to the prediction of Sommerfeld *et al.* From the general consideration we also concluded that there are no stable bound states or resonances in H^{2-} ions in the energy region studied.

This work is supported in part by U.S. Department of Energy, Office of Energy Research, Division of Chemical Sciences. T. M. acknowledges support by the REIMEI Research Fund of JAERI. C. G. B. is supported in part by the National Foundation of Natural Sciences of the People's Republic of China.

---

[1] D. S. Walton, B. Peart, and K. Dolder, J. Phys. B **3**, L148 (1970).
[2] D. S. Walton, B. Peart, and K. Dolder, J. Phys. B **4**, 1343 (1971).
[3] H. S. Taylor and L. D. Thomas, Phys. Rev. Lett. **28**, 1091 (1972).
[4] B. Simon, Int. J. Quantum Chem. **14**, 529 (1978).
[5] C. A. Nicolaides and D. R. Beck, J. Chem. Phys. **66**, 1984 (1977).
[6] C. A. Nicolaides and D. R. Beck, Int. J. Quantum Chem. **14**, 462 (1978).
[7] F. Robicheaux, R. P. Wood, and C. H. Greene, Phys. Rev. A **49**, 1866 (1994).
[8] L. H. Andersen *et al.*, Phys. Rev. Lett. **74**, 892 (1995).
[9] T. Tanabe *et al.*, Phys. Rev. A **54**, 4069 (1996).
[10] T. Sommerfeld, U. V. Riss, H.-D. Meyer, and L. S. Cederbaum, Phys. Rev. Lett. **77**, 470 (1996).
[11] T. Sommerfeld, U.V. Riss, H.-D. Meyer, and L. S. Cederbaum, Phys. Rev. A **55**, 1903 (1997).
[12] C. D. Lin, Phys. Rev. Lett. **35**, 1150 (1975).
[13] B. D. Esry, C. D. Lin, and Chris H. Greene, Phys. Rev. A **54**, 394 (1996).
[14] Yan Zhou and C. D. Lin, Phys. Rev. Lett. **75**, 2296 (1995).
[15] Xiazhou Yang, C. G. Bao, and C. D. Lin, Phys. Rev. Lett. **76**, 3096 (1996).
[16] G. W. F. Drake, Phys. Rev. Lett. **24**, 126 (1970).
[17] C. D. Lin, Phys. Rev. A **14**, 30 (1976).
[18] J. Z. Tang, C. D. Lin, B. Zhou, and Isao Shimamura, Phys. Rev. A **51**, 4694 (1995).
[19] B. F. Davis and K. T. Chung, Phys. Rev. A **42**, 5121 (1990).
[20] M. G. Sucre, F. Goychman, and R. Lefebvre, Phys. Rev. A **2**, 1738 (1970).
[21] J. H. Macek, J. Phys. B **1**, 831 (1968).
[22] C. G. Bao, X. Z. Yang, and C. D. Lin, Phys. Rev. A **55**, 4168 (1997).