SECOND BOUND STATE FOR THE HYDROGEN NEGATIVE ION*

G. W. F. Drake
Department of Physics, University of Windsor, Windsor, Ontario, Canada

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It is frequently stated that the $1s^2\,{}^1S$ state is the only bound state of H^-, although Holøien estimated that the $2p^2\,{}^3P$ state may also be bound. We show by a variational calculation that the $2p^2\,{}^3P$ state is definitely bound below the $n=2$ threshold of hydrogen. The best eigenvalue obtained is -0.125350 a.u.

The hydrogen negative ion (H^-) accounts for most of the long-wavelength continuous absorption in the solar atmosphere, while the reverse process of radiative attachment contributes to the continuous emission spectrum of high-current arc discharges (for reviews, see Branscomb[1,2]). It is often stated that the $1s^2\,{}^1S$ ground state is the only bound state of H^-, although Holøien[3] estimated by a semiempirical procedure that the $2p^2\,{}^3P$ state may also be bound by not more than 0.004 eV. We report in this Letter that the $2p^2\,{}^3P$ state of H^- is definitely bound below the $n=2$ excitation threshold and is one of the few firmly established bound excited states of negative ions. The problem is of theoretical interest because the hydrogen-atom core potential is asymptotically non-Coulombic and can support at most a finite number of bound states.[4]

The $2p^2\,{}^3P$ state of helium has long been recognized as a bound state imbedded in the autoionizing continuum and has been produced through electron impact by Burrow and Schulz.[5] The autoionization process is forbidden within the LS-coupling approximation because there is no overlapping continuum below the $n=2$ threshold of the correct angular momentum and parity. The $2p^2\,{}^3P$ state of H^- is similarly bound provided that it lies below the $n=2$ threshold at $E=-\frac{1}{8}$ a.u. A variational upper bound on the energy was obtained as follows.

Table I. H^- $2p^2\,{}^3P$ 22-term variational energy for various values of the scale factor β.

β	E (a.u.)
0.45	−0.1248335
0.40	−0.1249943
0.30	−0.1252329
0.22	−0.1253216
0.20	−0.1253310
0.18	−0.1253341
0.16	−0.1253266
0.14	−0.1252981
0.10	−0.1250816
0.05	−0.1248720
0.02	−0.1249780
$\beta\to 0$	−0.1250000

The nonrelativistic Schrödinger equation for H^- is

$$H\Psi_S=E_S\Psi_S, \qquad (1)$$

where

$$H=-\tfrac{1}{2}\nabla_1{}^2-\tfrac{1}{2}\nabla_2{}^2-1/r_1-1/r_2+1/r_{12}.$$

A variational approximation to $\Psi(2p^2\,{}^3P)$ was constructed by expansion in a correlated basis set of the form

$$\Psi=(1-P_{12})\sum_{i,j,k}a_{ijk}r_1{}^ir_2{}^jr_{12}{}^k \times\exp(-\alpha r_1-\beta r_2)\mathcal{Y}_{Ll_1l_2}{}^{M_L}(\hat{r}_1,\hat{r}_2),$$

where

$$\mathcal{Y}_{Ll_1l_2}{}^{M_L}(\hat{r}_1,\hat{r}_2)=\sum_{m_1,m_2}\langle l_1m_1l_2m_2|LM_L\rangle \times Y_{l_1}{}^{m_1}(\hat{r}_1)Y_{l_2}{}^{m_2}(\hat{r}_2), \qquad (2)$$

and P_{12} indicates the interchange of electrons 1 and 2. The integers i,j, and k were chosen such that $i\geq 1$, $j\geq 1$, $k\geq 0$, and $i+j+k\leq N$. The linear coefficients a_{ijk} were determined by solution of the secular problem, the scale factor α was set equal to its hydrogenic value 0.5, and β was adjusted to minimize the energy.

The energy is given as a function of β for the 22-term basis set in Table I. The energy clearly passes through a minimum in the neighborhood of $\beta=0.18$ and eventually tends to $-\frac{1}{8}$ a.u. as $\beta\to 0$. The apparent variational eigenvalue of an unbound state of H^- typically approaches −1/

$(2n^2)$ a.u. from above, as $\beta \to 0$, without exhibiting a minimum. The optimized energies are given for three basis sets in Table II. The lowest eigenvalue, $E = -0.125350$ a.u., is an upper bound and lies distinctly below the $n = 2$ threshold of hydrogen. The corresponding lower bound on the electron affinity is 0.0095 eV, which is a factor of 2.3 larger than the semiempirical estimate of Holøien.[3]

The optimum value of $\beta \simeq 0.18$ is suprisingly large and indicates that the state is more compact than one might expect. The root-mean-square radius $|\langle r_1^2 + r_2^2 \rangle|^{1/2}$ is 20.3 a.u., which is less than that of an $np\,^2P$ hydrogen atom in the $n = 4$ level. The state is not too large to exist even in relatively dense plasmas and may thus be observable.

The $2p^2\,^3P$ state of H^- may exist in significant quantities in the solar atmosphere. It can be formed by the radiative attachment of an electron to a hydrogen atom or by collisional excitation from the ground state of H^-. Once formed, the $2p^2\,^3P$ state can radiate either into the $1skp\,^3P$ continuum or to the $2s2p\,^3P$ autoionizing state with a lifetime of about 10^{-7} sec. Taking the position and width of the $2s2p\,^3P$ resonance to be 9.740 and 0.0006 eV, respectively,[6] the $2p^2\,^3P$-$2s2p\,^3P$ transition occurs at 3670 cm^{-1} with a width of about 50 cm^{-1}.

A similar calculation for the $2p3p\,^1P$ state did not produce a bound state in H^-. No other excited bound states are known to exist if one excludes autoionizing states. Results for the positions and radiative lifetimes of the $2p^2\,^3P$ and $2p3p\,^1P$ states of the remainder of the helium isoelectronic sequence will be presented in a forthcoming publication.

Table II. H^- $2p^2\,^3P$ variational energies.

No. of terms	E (a.u.)
22	−0.1253341
35	−0.1253395
50	−0.1253504

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SOME EVIDENCE FOR ADMIXTURE OF MAGNETIC QUADRUPOLE RADIATION IN ATOMIC X-RAY TRANSITIONS FROM MEASUREMENTS OF ANGULAR CORRELATION OF X RAYS

A. L. Catz
Department of Physics, University of Massachusetts,
Boston, Massachusetts 02116, and Arthur A. Noyes Nuclear Chemistry Center,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Angular correlations between K and L x rays in Pb were measured. The angular correlation functions for the K-L_α and K-L_β cascades were found to be $W(\theta) = 1 + (4.13 \pm 0.36) \times 10^{-2} P_2(\cos\theta)$ and $W(\theta) = 1 + (1.22 \pm 0.42) \times 10^{-2} P_2(\cos\theta)$, respectively. These results are in relatively good agreement with theoretical predictions only when the small admixtures of magnetic quadrupole radiation in the x-ray transitions are taken into account.

Allowed atomic x-ray transitions are generally considered to proceed by purely electric dipole radiation and the contributions to these transitions of radiations of higher multipolarity are usually overlooked. To the best knowledge of the author no such contributions have ever been experimentally demonstrated. However, the contribution of magnetic quadrupole radiation to the atomic x-ray transitions increases relative to the electric dipole contribution with increasing