The model, if valid, would best be applicable to the energy region in the spectrum of a composite particle above 100 MeV/nucleon. Unfortunately, no data exist at present in the appropriate range for the composite particles. It therefore would be interesting to have such data to see whether a high-energy thermal component is present, and if so, to use it to extract the thermal properties of the fireball.

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Proof that the H^- Ion Has Only One Bound State

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It is rigorously demonstrated that the nonrelativistic H^- ion has only one bound state in the fixed (infinite-mass) nucleus approximation with Coulomb interactions only.

The H^- ion, made up of a proton and two electrons, has long been known to have one bound state.[1] Additional bound states have never been found, but their nonexistence has so far not been proved. The present note provides the proof in the fixed (infinite-mass) nucleus approximation with Coulomb interactions only. The importance of the present result stems from the qualitative difference between the bound-state spectrum of negative ions (of which H^- is the simplest example) and the bound-state spectrum of positive ions and neutrals. Negative ions have only a finite number of bound states,[2] for which correlation effects are decisive (H^-, for example, is believed to have no bound states in Hartree-Fock approximation). Positive ions and neutrals, on the other hand, have an infinite number of bound states.[3]

The nonrelativistic Schrödinger equation for two electrons interacting with each other and with a fixed nucleus of charge Ze via Coulomb forces can be written in the form $H|\psi\rangle = E|\psi\rangle$, where $H = H_0 + V$, with

$$H_0(\vec{r}_1, \vec{r}_2; \vec{r}_1', \vec{r}_2') = (-V_1^2 - 2Zr_1^{-1} - V_2^2 - 2Zr_2^{-1})\delta(\vec{r}_1 - \vec{r}_1')\delta(\vec{r}_2 - \vec{r}_2') \tag{1}$$

and

$$V(\vec{r}_1, \vec{r}_2; \vec{r}_1', \vec{r}_2') = 2|\vec{r}_1 - \vec{r}_2|^{-1}\delta(\vec{r}_1 - \vec{r}_1')\delta(\vec{r}_2 - \vec{r}_2'). \tag{2}$$

Atomic units have been used and continuous matrix notation adopted for later convenience.

Proving the nonexistence of bound states requires a method which provides lower bounds to energy eigenvalues. The basic tool to be used here is a well-known comparison theorem.[4]

Theorem 1.—Let $H^{(1)}$ and $H^{(2)}$ be two Hermitian Hamiltonians whose discrete eigenvalues below the continuum can be characterized by the familiar variational principle $E = \min\langle\psi|H|\psi\rangle\langle\psi|\psi\rangle^{-1}$, with the minimization for excited states carried out subject to the constraint that $|\psi\rangle$ be orthogonal to preceding eigenvectors. Denote the ordered eigenvalues of $H^{(i)}$ by $E_1^{(i)} \leq E_2^{(i)} \leq \ldots \leq E_n^{(i)} \ldots \leq E_c^{(i)}$, where E_c is the energy at which the continuous spectrum (if any) begins. Then if $\langle\psi|H^{(1)}|\psi\rangle \leq \langle\psi|H^{(2)}|\psi\rangle$ holds for all admissible state vectors $|\psi\rangle$, $E_n^{(1)} \leq E_n^{(2)}$ holds for all n, and $E_c^{(1)} \leq E_c^{(2)}$. The result of the present paper will be obtained from theorem 1 by letting $H^{(2)} = H = H_0 + V$ while $H^{(1)}$ is something more tractable.

The lower-bounding Hamiltonian $H^{(1)}$ will be constructed by generalizing a method introduced by Bazley[5] to construct lower bounds to helium eigenvalues: Replace V in $H^{(2)} = H = H_0 + V$ by

$V^{1/2}PV^{1/2}$, where P is a projection operator. The positive square root of $2|\vec{r}_1-\vec{r}_2|^{-1}$ is to be taken when constructing $V^{1/2}$. The fact that a projection operator such as P cannot increase the length of a vector such as $V^{1/2}|\psi\rangle$ implies that $\langle\psi|V^{1/2}\times PV^{1/2}|\psi\rangle \leqslant \langle\psi|V|\psi\rangle$. The eigenvalues of $H^{(1)}=H_0+V^{1/2}PV^{1/2}$ are then lower bounds to the eigenvalues of H. Bazley constructed his $V^{1/2}PV^{1/2}$ by starting with the low-lying eigenvectors $|\xi_i\rangle$ of H_0 and using Schmidt orthogonalization to contruct vectors $|\xi_i'\rangle$ such that $\langle\xi_i|V^{-1}|\xi_i'\rangle=\delta_{i,j}$. His $V^{1/2}PV^{1/2}$ then took the form

$$V^{1/2}PV^{1/2}=\sum_{i=1}^{N}|\xi_i'\rangle\langle\xi_i'|$$

for small finite N.

The discrete spectrum of H_0, given by

$$E_{n_1,n_2}{}^{(0)}=-Z^2(n_1{}^{-2}+n_2{}^{-2}), \tag{3}$$

where (n_1,n_2) is any pair of positive integers, is known from the theory of the hydrogen atom. Because the two-electron system can dissociate into a free electron plus an electron bound in a hydrogenic ground state with energy $-Z^2$, both H_0 and $H=H_0+V$ have a continuous spectrum beginning at $-Z^2$.[6] The spectrum (3) has an infinite number of levels belonging to pairs of quantum numbers of the form $(1,n_2)$ and $(n_1,1)$ which lie below $-Z^2$ and accumulate at $-Z^2$. In order to prove that $H=H_0+V$ has only one bound state for $Z=1$, $V^{1/2}PV^{1/2}$ must contain enough of the original repulsive V to push all but one of these levels up to -1; in particular $V^{1/2}PV^{1/2}$ must couple to all of these levels of H_0 which lie below the continuum. Stated another way, $V^{1/2}PV^{1/2}$ must retain enough of the original V to preserve shielding: If one electron is in a hydrogenic ground state with the second electron far out, the far-out electron must see, after the replacement of V by $V^{1/2}PV^{1/2}$, a potential which cannot support an infinite number of bound states. The Schmidt orthogonalization used by Bazley[5] to construct his $V^{1/2}PV^{1/2}$ will clearly not work here, because it produces a $V^{1/2}PV^{1/2}$ which couples only a finite number of low-lying states of H_0.

A suitable $V^{1/2}PV^{1/2}$ for use in the lower-bounding Hamiltonian $H^{(1)}=H_0+V^{1/2}PV^{1/2}$ can be constructed by introducing

$$V_1(\vec{r}_1,\vec{r}_2;\vec{r}_1{}',\vec{r}_2{}')\equiv U(r_1)\delta(\vec{r}_1-\vec{r}_1{}')\varphi_1(r_2)\varphi_1{}^*(r_2{}') \tag{4}$$

and

$$V_2(\vec{r}_1,\vec{r}_2;\vec{r}_1{}',\vec{r}_2{}')\equiv \varphi_1(r_1)\varphi_1{}^*(r_1{}')U(r_2)\delta(\vec{r}_2-\vec{r}_2{}'), \tag{5}$$

where

$$\varphi_1(r)=Z^{3/2}\pi^{-1/2}\exp(-Zr) \tag{6}$$

is the normalized hydrogenic ground-state wave function and

$$U(r)\equiv[\int \tfrac{1}{2}|\vec{r}-\mathrm{r}'||\varphi_1(r')|^2 d^3r']^{-1}. \tag{7}$$

V_1 can be obtained by applying Bazley's Schmidt orthogonalization procedure to vectors which are eigenfunctions of the position operator in $\vec{r}_1$ and hydrogenic ground-state functions in $\vec{r}_2$. Both $P_1=V^{-1/2}\times V_1V^{-1/2}$ and $P_2=V^{-1/2}V_2V^{-1/2}$ are projection operators. Neither V_1 nor V_2 alone couples to all levels of H_0 below the continuum, but $V^{1/2}PV^{1/2}$ *will* couple to all levels of H_0 below the continuum (actually, to everything below $-Z^2/2$) if P is chosen to be the projection onto the span of the ranges of P_1 and P_2. This P is given by

$$P=\tfrac{1}{2}(P_1+P_2)+\tfrac{1}{2}\sum_{n=0}^{\infty}\sum_{i=1}^{2}(I-P_i)P_{3-i}K_i{}^nP_{3-i}(I-P_i), \tag{8}$$

where K_i is the Hilbert-Schmidt kernel

$$K_i=P_{3-i}P_iP_{3-i} \tag{9}$$

and I is the identity operator. It is straightforward to verify that P is Hermitian, that $PP_1=P_1P=P_1$, that $PP_2=P_2P=P_2$, and that $P^2=P$.

Convergence of the infinite series of operators in P is implied by the following observations. (1) Since K_i is a product of projection operators, its eigenvalues cannot exceed 1. (2) Eigenvectors of K_i with eigenvalue 1 must be simultaneous eigenvectors of the projection operators P_1 and P_2. (3) Such simultaneous eigenvectors are annihilated by $(I-P_i)P_{3-i}$ and its adjoint. (4) Since K_i is Hilbert-Schmidt, its eigenvalues cannot accumulate at 1. Thus only eigenvalues of K_i which are strictly less than 1 contribute to the sum in P, which therefore converges by comparison with the geometric series.

It should be noted that the terms in the sum in P have either the form A^+A or the form A^+QA, where Q is a projection operator. Expectation values of such terms cannot be negative. Thus lower bounds to the eigenvalues of $H=H_0+V$ are obtained even if all but a finite number of the terms in the infinite sum in P are discarded.

The eigenvalue problem for $H_0+V^{1/2}PV^{1/2}$ is simpler than the eigenvalue problem for $H=H_0+V$. Let $\mathcal{S}_S$ be the space spanned by functions of the form

$$\psi_S(\vec{r}_1,\vec{r}_2)=f(\vec{r}_1)\varphi_1(r_2)+\varphi_1(r_1)f(\vec{r}_2), \tag{10}$$

$\mathcal{S}_A$ the space spanned by functions of the form

$$\psi_A(\vec{r}_1,\vec{r}_2)=g(\vec{r}_1)\varphi_1(r_2)-\varphi_1(r_1)g(\vec{r}_2), \tag{11}$$

and $\mathcal{S}_\perp$ the orthogonal complement of $\mathcal{S}_A \cup \mathcal{S}_S$. Each of the spaces $\mathcal{S}_A$, $\mathcal{S}_S$, and $\mathcal{S}_\perp$ is mapped into itself by $H_0+V^{1/2}PV^{1/2}$. $V^{1/2}PV^{1/2}$ is zero on $\mathcal{S}_\perp$, so that eigenfunctions in $\mathcal{S}_\perp$ have their eigenvalues given by (3) with $n_1 \geqslant 2$, $n_2 \geqslant 2$. All of these lie above $-Z^2/2$ and are therefore not relevant here.

The eigenvalue problems for $H_0+V^{1/2}PV^{1/2}$ on $\mathcal{S}_S$ and $\mathcal{S}_A$ are equivalent to the following one-particle eigenvalue problems for f and g:

$$\{h_0-ZV_0+U+[\tfrac{1}{2}Z^2-(16Z/35)]|\varphi_1\rangle\langle\varphi_1|+\sum_{n=1}^{\infty}U^{1/2}M^nU^{1/2}\}|f'\rangle=(E+Z^2)(I-\tfrac{1}{2}|\varphi_1\rangle\langle\varphi_1|)|f'\rangle, \tag{12}$$

where

$$|f'\rangle \equiv (I+|\varphi_1\rangle\langle\varphi_1|\rangle)|f\rangle \tag{13}$$

and

$$(I-|\varphi_1\rangle\langle\varphi_1|)\{h_0-ZV_0+U+\sum_{n=1}^{\infty}U^{1/2}(-M)^nU^{1/2}\}(I-|\varphi_1\rangle\langle\varphi_1|)|g\rangle=(E+Z^2)(I-|\varphi_1\rangle\langle\varphi_1|)|g\rangle. \tag{14}$$

Here

$$h_0(\vec{r},\vec{r}\,')=-\nabla^2\delta(\vec{r}-\vec{r}\,'), \tag{15}$$

$$V_0(\vec{r},\vec{r}\,')=2r^{-1}\delta(\vec{r}-\vec{r}\,'), \tag{16}$$

I is the identity, and $|\varphi_1\rangle$ and U are given by (6) and (7), respectively. M is the Hilbert-Schmidt kernel

$$M(\vec{r},\vec{r}\,')=h_1(r)h_1(r')-k(\vec{r},\vec{r}\,'), \tag{17}$$

where

$$k(\vec{r},\vec{r}\,')\equiv\tfrac{1}{2}[U(r)]^{1/2}\varphi_1(r)|\vec{r}-\vec{r}\,'|\varphi_1{}^*(r')[U(r')]^{1/2} \tag{18}$$

and

$$h_1(r)=(32Z)^{1/2}[35U(r)]^{-1/2}\varphi_1(r). \tag{19}$$

It is straightforward to verify that h_1 is a normalized eigenfunction of the kernel k with eigenvalue 1. The following argument shows that all eigenvalues of M are nonnegative: The kernel k has the representation $k=k_1-k_2$, where

$$k_1(\vec{r},\vec{r}\,')=\tfrac{1}{4}[U(r)]^{1/2}\varphi_1(r)(1+r)(1+r')\varphi_1{}^*(r')[U(r')]^{1/2} \tag{20}$$

and

$$k_2(\vec{r},\vec{r}\,')=\tfrac{1}{4}[U(r)]^{1/2}\varphi_1(r)\{(1-r)(1-r')+\pi^{-1}\int(|\vec{r}-\vec{r}\,''|^{-1}-r^{-1})(|\vec{r}\,'-\vec{r}\,''|^{-1}-r'^{-1})d^3r''\}\times\varphi_1{}^*(r')[U(r')]^{1/2} \tag{21}$$

are integral operators with nonnegative expectation values. Theorem 1 implies that the eigenvalues of k are bounded above by the eigenvalues of k_1. But k_1 has only one positive eigenvalue. Hence k has only one positive eigenvalue, which must be the eigenvalue 1 associated with the eigenfunction h_1. Therefore all eigenvalues of M are nonnegative. This fact plus theorem 1 implies that the eigenvalues of

$$[h_0-\lambda(V_0-U)]|f'\rangle=(E+1)(I-\tfrac{1}{2}|\varphi_1\rangle\langle\varphi_1|)|f'\rangle \tag{22}$$

and

$$(I - |\varphi_1\rangle\langle\varphi_1|)[h_0 - \lambda(V_0 - U + U^{1/2}MU^{1/2})](I - |\varphi_1\rangle\langle\varphi_1|)|g\rangle = (E+1)(I - |\varphi_1\rangle\langle\varphi_1|)|g\rangle \tag{23}$$

for $\lambda = 1$ are lower bounds to the eigenvalues of (12) and (14) for $Z = 1$ (for H^-). Equations (22) and (23) are obtained from (12) and (14), respectively, by setting $Z = 1$ and discarding terms whose expectation values are nonnegative.

The number of bound states of (22) and (23) can be counted by the standard trick of sitting at the bottom of the continuum, cranking up the coupling constant λ, and counting the bound states as they come in.[7] One sets $E = -1$ and lets λ be the eigenvalue; the number of eigenvalues λ which do not exceed 1 is then the same as the number of bound states for $\lambda = 1$. Since (22) and (23) are spherically symmetric, one-particle equations, the number of eigenvalues λ which do not exceed 1 can be counted by decomposing in partial waves and using standard methods for one-dimensional problems. In this way it can be shown that (22), and therefore also (12) and the singlet state of H^-, has one bound state, while (23), and therefore also (14) and the triplet state of H^-, has none.

The methods outlined here can also be used to calculate lower bounds to those bound states of two-electron atomic systems which do exist. Numerical results of such calculations and additional details of the present proof will be published elsewhere.

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