The Stability of Three-Body Atomic and Molecular Ions

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Chemistry has all to do with *binding*, superficially with the binding of atoms and ions to form molecules and crystals, and more fundamentally with the binding of negatively charged electrons and positively charged nuclei. The simplest chemical molecule is the hydrogen molecular ion H_2^+, consisting of two protons (p^+) bound together in its ground state by a single electron (e^-), that is, $p^+e^-p^+$. Another three-particle ion of great importance in chemistry and astrophysics is the hydride, or negative hydrogen ion, H^-, which consists of two electrons bound by a single proton, that is, $e^-p^+e^-$. In contrast to H_2^+, which has a large number of bound states in which neither of the protons can escape to infinity leaving behind an H atom, H^- has a much more marginal existence, having only two bound states, a weakly bound singlet ground state and an even more weakly bound triplet excited state.

Nowadays the number of three-particle ions of interest has greatly increased because of the relative ease of production of deuterons and tritons (d^+ and t^+), of muons (μ^+ and μ^-), and of antiparticles such as the positron (e^+) and antiproton (p^-). Thus new branches of chemistry of short-lived atoms and ions have grown up based on positronium (Ps = e^+e^-), muonium (Mn = μ^+e^-), and protonium (Pn = p^+p^-) and its isotopes. Not all the ions of these species exist, that is, have one or more stable states with energies lower than those of the most stable ion pair. For example, the protonium ion Pn^- ($=e^-p^+p^-$) and the ion e^+H ($=e^+e^-p^+$) do not exist, but the positronium ions Ps^- ($=e^-e^+e^-$) and mesic-H_2^+ ($=p^+\mu^-p^+$) do exist, and indeed the lifetime of Ps^- was measured by Mills[1] in 1981, 35 years after its existence was first predicted by Wheeler.[2]

There are 36 different singly-charged ions made up of e, μ, and p particles and antiparticles, of which 16 have distinct mass ratios. If d and t are included, the number is 150, of which 71 have distinct mass ratios. It is not at all obvious which of these ions are stable and which are not. A few of them are of great interest for muon-catalyzed nuclear fusion, in particular the isotope of mesic-H_2^+, $d^+\mu^-t^+$, which has a weakly bound excited state with energy 0.66 eV which plays a crucial role in the muon-catalyzed fusion cycle.[3] The subject is thus not only of academic interest, and the object of this Account is to attempt to formulate the stability problem in the simplest way, to describe the main results that have been achieved so far, and to propose a simple stability diagram (which should appeal to chemists) to systematize the results.

Critical Binding Energy

The existence or otherwise of a stable state clearly depends on the masses of the three particles. Let us consider the general case of three subatomic particles of masses m_1, m_2, and m_3, each having unit electronic charge e with one, say particle 2, having opposite sign from the other two. The energy and binding will not be affected by the sign of the charge, which we take to be negative. The three-particle ion therefore has a net positive charge and can be written $m_1^+m_2^-m_3^+$. With no loss of generality we can take particle 1 to be the lighter of the pair 1,3, so that $m_1 \leq m_3$. This means that if the trio is marginally unstable it will break up into the heavier bound pair 2,3 ($m_2^-m_3^+$) and the isolated particle 1 at rest at infinity, since the energy of a two-body Coulombic system is proportional to its reduced mass (see below).

We can now define the binding energy ΔE of the ion by

$$\Delta E = E_{\text{ion}}(m_1,m_2,m_3) - E_{\text{thr}}(m_2,m_3) \qquad (1)$$

where the ground-state energy of the two-body "atom" 2,3 is given by nonrelativistic quantum mechanics as

$$E_{\text{thr}}(m_2,m_3) = -\frac{\mu_{23}e^4}{2\hbar^2} \qquad (2)$$

where $\hbar$ is the Dirac constant (Planck's constant $h/2\pi$) and μ_{23} is the reduced mass of 2,3 given by

$$1/\mu_{23} = 1/m_2 + 1/m_3 \qquad (3)$$

For stable binding, $\Delta E < 0$, and for critical binding, $\Delta E = 0$.

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The three-particle energy $E_{ion}(m_1,m_2,m_3)$ appearing in eq 1 is the lowest eigenvalue of the Hamiltonian $\hat{H}$ of the system corresponding to zero total linear and angular momenta, where

$$\hat{H} = -\frac{\hbar^2}{2m_2}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 - \frac{\hbar^2}{2m_3}\nabla_3^2 - \frac{e^2}{r_{12}} - \frac{e^2}{r_{23}} + \frac{e^2}{r_{31}} \quad (4)$$

The Schrödinger equation for this Hamiltonian cannot be solved analytically, any more than the classical equations of motion for three bodies interacting with Coulombic or gravitational forces can be solved exactly. However, recently the advent of high-speed computers has opened up a whole new approach to these problems by making it possible to solve the quantal and classical equations numerically for given masses to a very high degree of accuracy. Nevertheless, the computational effort involved is such that the critical mass ratios at which bound states appear have not yet been established. Despite the lack of definitive results, a lot of progress can be made in understanding the problem by using general relationships and considering a few special cases.

Ternary Stability Diagram

It follows from eq 1 and the Hamiltonian 4 that the stability limits depend only on the ratio of the masses, and not on their absolute values. It can also be seen from eq 4 that the mass parameters which occur linearly in the Hamiltonian are not the masses themselves but their reciprocals, $1/m_1$, $1/m_2$, and $1/m_3$. These considerations suggest that the most appropriate parameters for describing the mass composition of a three-particle ion are the *reciprocal mass fractions* defined by

$$x_1 = \mu/m_1,\ x_2 = \mu/m_2,\ x_3 = \mu/m_3 \quad (5)$$

where

$$1/\mu = 1/m_1 + 1/m_2 + 1/m_3 \quad (6)$$

It follows that only two of the x's are independent since

$$x_1 + x_2 + x_3 = 1 \quad (7)$$

It is well-known that in chemical thermodynamics the variations in concentration of three-component mixtures can be conveniently expressed by means of a triangular or *ternary* diagram (see, for example, Bowden,[4] Prigogine and Defay,[5] and Martin et al.[6]). In the most popular method the composition of the mixture is represented by a point within an equilateral triangle of unit side. The vertices of the triangle correspond to the pure components, say 1, 2, and 3. The fraction x_1 of the first component is equal to the distance of the point from the side 23 along a line parallel to side 12. Elementary geometry ensures that the sum of the fractions satisfies eq 7.

Note that in the notation of Martin et al.[6] particles 2 and 3 have the same charge. Also, for a given point on their diagram, $x_i = \alpha_i$ is taken to be the *perpendicular* distance of the point from the side jk ($j \neq i, k \neq i$); in this case the sides of the equilateral triangle have to be of length $2/3^{1/2}$ units for eq 7 to be satisfied.

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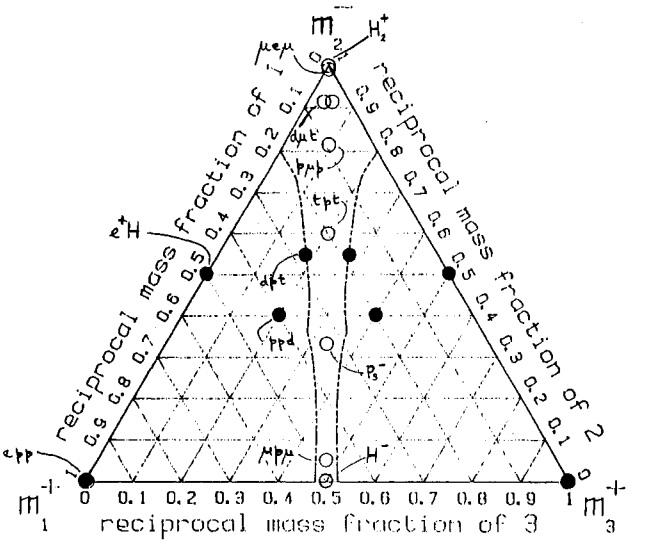

Figure 1. Reciprocal mass fraction ternary diagram for three-particle ions $m_1^+m_2^-m_3^+$ (or $m_1^-m_2^+m_3^-$), showing systems which are stable according to Poshusta[22] as open circles, and those not possessing a bound state as solid circles. The dashed and dotted lines are Poshusta's variational estimate of the critical binding curves.

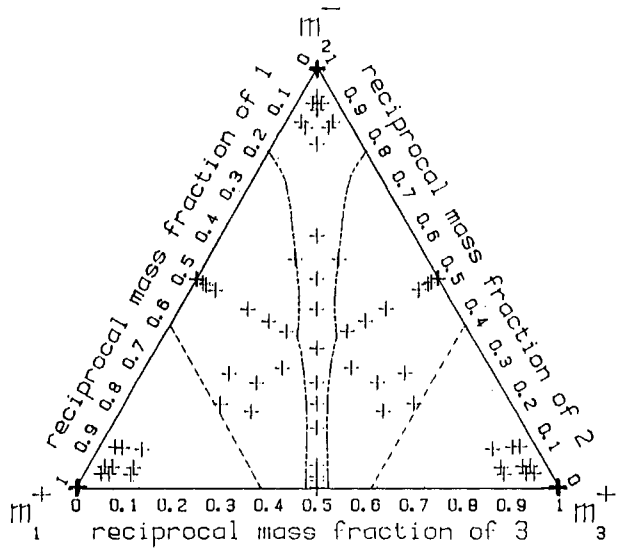

Figure 2. Reciprocal mass fraction ternary diagram for three-particle ions $m_1^+m_2^-m_3^+$ (or $m_1^-m_2^+m_3^-$) showing all possible systems composed of e, μ, p, d, and t as crosses. The two straight dashed lines are the critical binding curves predicted by a crude argument based on the critical dipole moment to bind a particle.

We can use such a ternary diagram with reciprocal mass fractions defined by eq 6 to represent the relative composition by mass of any three-particle ion m_1^+-$m_2^-m_3^+$. Thus vertex 1 corresponds to particles 2 and 3 being infinitely massive compared to 1, while side 13 corresponds to particle 2 being infinitely massive compared to 1 and 3, and so on. Figure 1 shows a diagram of this type with small labeled circles to indicate the mass compositions of some of the well-known or interesting ions. In Figure 2 the crosses indicate all three-particle ions made up of e, μ, p, d, and t. Note that the diagrams are symmetrical about the altitude through m_2^-, corresponding to the interchange of m_1^+ and m_3^+. We shall refer to this altitude as the symmetry axis of the diagram.

A very rough but illuminating argument can be given to suggest the areas of binding on the diagram, based

on the critical dipole for binding an electron calculated by Byers Brown and Roberts[7] and others.[8-10] Consider the case when m_2^- and m_3^+ are sufficiently larger than m_1^+ that we can use the Born–Oppenheimer approximation for the motion of m_1^+ in the field of $m_2^-m_3^+$. If we neglect m_1^+, $m_2^-m_3^+$ will move around their center of mass with an average separation (and hence instantaneous dipole moment) of $1/\mu_2 = 1/m_2 + 1/m_3$, in atomic units ($e = \hbar = m_e = 1$). Now the critical value of the dipole to bind a particle of mass m_1 with electronic charge is $D \geq 0.639/m_1$.[7-10] Equating these two, we get

$$1/m_2 + 1/m_3 \geq \frac{0.639}{m_1}$$

or

$$x_2 + x_3 \geq 0.639x_1$$

or

$$x_1 \leq 0.610$$

Thus, according to this argument, the system will be bound if $x_1 \leq 0.610$ or, if we interchange m_1^+ and m_3^+, $x_3 \leq 0.610$. The critical values lie on the straight lines represented by dashes on Figure 2.

General Properties of the Boundary of the Region of Stability

Two general properties of the boundary of the region of stability have recently been established by Martin et al.[5]

(i) A Straight Line on the Ternary Stability Diagram from a Lower Corner of the Diagram to the Symmetry Axis Crosses the Boundary at Most Once. The proof of this result is straightforward. If (m_1, m_2, m_3) is stable with $m_3 > m_1$ (say), then if m_1 increases with m_2 and m_3 unchanged, the threshold energy, $E_{thr}(m_2,m_3)$, remains constant. However, it follows, from the lower bound property of the ground-state energy (see, for example, Pauling and Wilson[11] and Bransden and Joachain[12]) and the fact that kinetic energy expectation values are always positive, that E_{ion}-(m_1,m_2,m_3) must decrease, thus increasing the stability of the system. In terms of the reciprocal mass fractions, $\{x_i\}$, increasing m_1 while keeping m_2 and m_3 constant corresponds to decreasing x_1 while keeping x_2/x_3 constant. Also $m_3 > m_1$ implies that $x_3 < x_1$. It follows that, on the ternary diagram, increasing m_1 while keeping $m_1 < m_3$ and m_2 and m_3 constant corresponds to motion to the right along a straight line from the left lower corner of the diagram to some point on the symmetry axis.

The result we have deduced about the increase in stability shows that once such a line enters the region of stability, it can never leave it. It follows from the symmetry of the diagram that this must also hold for a straight line from the right lower corner to some point on the symmetry axis.

(ii) Each Half of the Region of Instability is Convex. That Is, Apart from Its End Points, the Straight Line Joining Any Two Points on the Boundary of the Region of Stability Lies Entirely within the Region of Instability. The proof of this result is more difficult, and the interested reader is referred to the paper by Martin et al.[5]

As these authors point out, the rigorous results i and ii do not exclude the possibility that the stability region could consist of two separated domains, with a hole of instability near the center of the triangle. However, the proof by Hill[13] that every system that lies on the symmetry axis (i.e., $m_1 = m_3$) is stable demonstrates that the stability region must take the form of a connected band in the middle of the ternary diagram.

Methods for Obtaining Information about Bound States of the Three-Body System

(i) The Rayleigh–Ritz Variational Method. If we separate off the center of mass motion (see, for example, Bransden and Joachain[14]) and take the origin to be at particle 3 (say), in atomic units the Hamiltonian, $\hat{H}_{int}$, for the internal motion of the three particles takes the form

$$\hat{H}_{int} = -\frac{1}{2\mu_{13}}\nabla_{\mathbf{r}_1}^2 - \frac{1}{2\mu_{23}}\nabla_{\mathbf{r}_2}^2 - \frac{1}{m_3}\nabla_{\mathbf{r}_1}\cdot\nabla_{\mathbf{r}_2} + \frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{r_{12}} \quad (8)$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of particles 1 and 2, respectively, with respect to the third particle as origin. The Hamiltonians 4 and 8 are equivalent if the total linear momentum of the ion is 0. $\hat{H}_{int}$ represents the motion of two particles (more properly, pseudoparticles) of mass μ_{13} and μ_{23}, respectively. It differs from the usual form for the Hamiltonian for two particles as it contains a coupling term between the momenta of the particles. This is known as the Hughes–Eckart or mass polarization term (Hughes and Eckart,[15] Bethe and Salpeter,[16] and Bransden and Joachain[14]). If desired, it can be eliminated by transforming to Jacobi coordinates (see, for example, Messiah[17]). Any eigenfunction of $\hat{H}_{int}$ for which $E_{ion} < E_{thr}$ will be square-integrable.[18] We define such a state to be a bound state. As was pointed out earlier, no exact solution exists to the problem of quantum mechanical motion with the Hamiltonian, $\hat{H}_{int}$. However, the Rayleigh–Ritz variational method (see, for example, Pauling and Wilson[11] and Bransden and Joachain[12]), which is very widely used in quantum chemistry, can often be used to prove the existence of a bound state. More generally, the Hylleraas–Undheim theorem[11,12,19] makes it possible to use the variational method to obtain a lower bound on the number of bound states, N_b. It follows from this theorem that if there are n approximate eigenfunctions with energy expectation values below E_{thr}, then

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$$N_b \geq n \tag{9}$$

However, it cannot give an upper bound on N_b. In particular, the method fails completely if, despite all efforts to make the trial function as flexible as possible, n is found to be 0.

It has been possible to show using this method that bound states exist for many three-body Coulombic systems. Once a bound state has been shown to exist, the method can then be used to obtain an accurate energy and wave function for the bound state. Thus the method has been successfully applied to H_2^+ and related isotopes (see, for example, Bates et al.,[20] Kołos et al.,[21] and Poshusta[22]), H^- and related isotopes (see, for example, Bethe,[23] Hylleraas,[24] Pekeris,[25] and Frolov and Yeremin[26]), $e^-e^+e^-$ (see, for example, Wheeler,[2] Kołos et al.,[21] Ho,[27] Bhatia and Drachman,[28] Frolov,[29,30] Petelentz and Smith,[31] and Frolov and Yeremin[26]), and several three-body systems involving a muon or an artificial particle (see, for example, Kołos et al.,[21] Bhatia and Drachman,[32,33] Hu,[34] Frolov,[29] Hara et al.,[35] Petelentz and Smith,[31,36] Korobov et al.,[37] Kamimura,[38] Scrinzi et al.,[39] and Frolov and Yeremin[26]).

An interesting case in which the variational method fails is e^+H. However, Inokuti et al.[40] were able to show by this method that if the mass, m_3, of the proton is taken to be infinite, a "positron" of mass $m_1 \geq 7.8m_e$ where $m_2 = m_e$ is the mass of the electron, would be bound.

Frost et al.[41] reduced this upper bound to $2.625m_e$ by using a more flexible trial function. It was reduced still further to $2.20m_e$ by Rotenberg and Stein.[42] They made their trial function even more flexible by including basis functions suitable for representing a weakly bound particle in a potential with the appropriate asymptotic form for an H atom and a positron (see, for example, Bransden and Joachain[43]),

$$V(r_1)_{r_1 \to \infty} \sim -\alpha/2r_1^4 \tag{10}$$

where α is the dipole polarizability of the H atom.

The overall system has been studied for general m_2/m_1 and m_1/m_3 by Poshusta[22] using the variational method with basis sets made up of Singer-type geminal functions (Singer[44]). His results give a good overall picture of the region of stability in which at least one bound state exists. However, a variational calculation necessarily underestimates this region. This underestimation is increased to some extent, by his use of Singer-type geminal functions. They are Gaussian-type functions and are not as well-suited for taking into account the Coulombic interaction as the Hylleraas-type functions used in highly accurate calculations of three-body Coulombic systems.

The two dashed and dotted curves on Figures 1 and 2 indicate the boundary of the region of stability as calculated by Poshusta[22] using the variational method. Points in the central region between the curves represent systems which have at least one bound state. The kink in each curve is an artifact of Poshusta's plotting procedure. We can see that the boundary obtained by using the critical dipole argument is quantitatively correct.

$H_2^+, \mu^+e^-\mu^+, p^+\mu^-p^+, d^+p^-d^+, t^+p^-t^+, Ps^-, \mu^+p^-\mu^+, e^-\mu^+e^-$, and H^- are all systems for which the two particles which have the same charge also have the same mass. They thus lie on the altitude through m_2^-, about which the region of stability is symmetrical. Hill's work[13] described earlier shows that they must all have at least one bound state. $p^+\mu^-d^+$ and $d^+\mu^-t^+$ are examples of systems which lie within the calculated region of stability whereas $d^+p^-t^+$, $p^+p^-d^+$, $e^+\mu^-\mu^+$, $e^-p^+\mu^-$, and $e^+\mu^-p^+$ are examples of systems which do not. However, $d^+p^-t^+$ is very close to the boundary and Poshusta considers it is probably within the true region of stability. This has indeed been shown to be the case recently by Frolov and Thakkar[45] using the variational method and a trial function made up of terms which are exponential in each of the interparticle distances. By contrast, $p^+p^-d^+$ is quite deep in the unstable region and probably does not lie in the true region of stability.[22]

(ii) Determination of Lower Bounds to the Eigenvalues of the System. Suppose the variational method fails because no approximate eigenfunction is obtained with energy expectation value less than E_{thr}. The absence of a bound state can still be proved if a lower bound to the lowest eigenvalue of the system is obtained and this lower bound is not less than E_{thr}. More generally, if an upper bound on the number of bound states is required, a lower rather than an upper bound to the eigenvalues of the system is required. This is, in general, much more difficult to obtain (Spruch[46]).

It is usually done by making use of the comparison theorem (see, for example, Hill[13]). This theorem states that if two Hamiltonians $\hat{H}_1$ and $\hat{H}_2$ are such that

$$\langle \Psi|\hat{H}_1|\Psi\rangle \leq \langle \Psi|\hat{H}_2|\Psi\rangle \tag{11}$$

for any allowed square-integrable function Ψ, then

$$E_{thr}^{(1)} \leq E_{thr}^{(2)} \tag{12}$$

where $E_{thr}^{(i)}$ is the energy at which the continuum threshold (if any) of $\hat{H}_i$ begins. Also, if $\hat{H}_1$ and $\hat{H}_2$ have at least n bound states and the mth bound state of $\hat{H}_i$

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has energy $E_m^{(i)}$, then

$$E_m^{(1)} \leqslant E_m^{(2)} \qquad m \leqslant n \tag{13}$$

In addition, if

$$E_{\text{thr}}^{(1)} = E_{\text{thr}}^{(2)} \tag{14}$$

and $\hat{H}_1$ has exactly n bound states, then n is an upper bound to the number of bound states of $\hat{H}_2$.

In practical applications of this theorem, $\hat{H}_2$ is taken to be the original Hamiltonian for the problem, while $\hat{H}_1$ is the Hamiltonian of a more tractable system. Using the variational method described earlier, Hill[13] was able to prove that Coulombic systems with $m_1 = m_3$ always have at least one bound state, irrespective of the value of m_2. By taking $\hat{H}_2$ to be $\hat{H}_{\text{int}}$ with origin at particle 2 and $\hat{H}_1$ a Hamiltonian for which the Schrödinger equation is reducible to one-particle equations, he was able to prove further that these systems have only one bound state if $m_2/m_1 < 0.210\,106\,36$.

It follows from the above theorem that if eq 4 holds and $\hat{H}_1$ has no bound states, then $\hat{H}_2$ also has no bound states. This result was used by Spruch[46] to devise a method for showing that no bound state of the e^+H system exists if the mass of the proton is taken to be infinite.

In this case $\hat{H}_{\text{int}}$ is as in eq 8 and can thus be expressed in the form

$$\hat{H}_{\text{int}} = -\frac{1}{2m_1}\nabla_{\mathbf{r}_1}^2 + \frac{1}{r_1} + \hat{H}_e \tag{15}$$

where

$$\hat{H}_e = -\frac{1}{2m_2}\nabla_{\mathbf{r}_2}^2 - \frac{1}{r_2} - \frac{1}{r_{12}} \tag{16}$$

is the Hamiltonian for an electron in the field of two equal, fixed positive charges, one at the origin and the other at $\mathbf{r}_1$. Now $\hat{H}_e$ is just the Hamiltonian which determines the electronic potential energy of the H_2^+ ion in the Born–Oppenheimer approximation (see, for example, Pauling and Wilson[47] and Bransden and Joachain[48]). The associated Schrödinger equation is separable in prolate spheroidal (confocal elliptical) coordinates. The eigenvalues of $\hat{H}_e$ are functions only of r_1, and the separability of the Schrödinger equation makes it possible to calculate them to high accuracy (Bates et al.[20] and Wind[49]).

Let us consider the adiabatic Hamiltonian

$$\hat{H}_{\text{ad}} = \hat{I}(\mathbf{r}_2)\hat{H}_p \tag{17}$$

where

$$\hat{H}_p = -\frac{1}{2m_1}\nabla_{\mathbf{r}_1}^2 + \frac{1}{r_1} + E_0(r_1) \tag{18}$$

and $\hat{I}(\mathbf{r}_2)$ is the unit operator for allowed square-integrable functions of $\mathbf{r}_2$ and $E_0(r_1)$ is the ground-state eigenvalue of $\hat{H}_e$. It is referred to as adiabatic because the potential term, $E_0(r_1)$, is calculated by fixing $\mathbf{r}_1$ and then calculating the ground-state energy of the electron in the resulting two-center attractive Coulombic potential.

It is easy to show that $\hat{H}_1 = \hat{H}_{\text{ad}}$ and $\hat{H}_2 = \hat{H}_{\text{int}}$ as above satisfy eqs 11 and 14. The proof of eq 11 is similar to Epstein's proof that the ground-state energy of a molecule in the adiabatic approximation is a lower bound to the true energy of the ground state. Hence if no bound state of $\hat{H}_{\text{ad}}$ exists, no bound state of $\hat{H}_{\text{int}}$ exists. It is usual to adjust the potential in an essentially one particle Hamiltonian such as $\hat{H}_{\text{ad}}$ so that it tends to 0 as r_1 tends to infinity. Thus the problem of showing that $\hat{H}_{\text{ad}}$ and hence $\hat{H}_{\text{int}}$ have no bound states reduces to the problem of showing that the potential, $V(r)$, cannot support a bound state, where

$$V(r) = \frac{1}{r} + E_0(r) - E_{\text{H}}^{(0)} \tag{19}$$

and

$$E_{\text{H}}^{(0)} = \lim_{r\to\infty} E_0(r) = \text{ground-state energy of H} = -\frac{1}{2}m_2$$

$V(r)$ is a central potential, i.e., it is spherically symmetric. Though it depends on the single radial variable, r, it is a potential in three dimensions. This is very important. Any attractive well potential can bind a particle in one dimension (see, for example, Landau and Lifshitz[51]), but in three dimensions it has to exceed a critcal strength to produce binding (see, for example, Dyson[52] p 1225, and Wu and Ohmura[53]).

Ways of calculating the number of bound states which $V(r)$ can support have been extensively studied (Bargmann[54] and Schwinger[55]). As $V(r) \to 0$ more rapidly than r^{-2} as $r \to \infty$ and behaves like r^{-1} as $r \to 0$, a necessary but *not* sufficient condition for $V(r)$ to be able to support $N_b^{(l)}$ bound states corresponding to angular momentum l for a particle of mass m is that

$$N_b^{(l)} \leqslant \frac{2m}{(2l+1)\hbar^2}\int_0^\infty r[-V_-(r)]\,dr \tag{20}$$

where

$$V_-(r) = V(r) \qquad V(r) \leqslant 0$$

$$V_-(r) = 0 \qquad V(r) > 0$$

This is usually referred to as the Bargmann–Schwinger result.[46] Also, important information about the number of bound states can be obtained by an analysis of the phase shift of particles of mass m scattered by $V(r)$ (see, for example, Burke[56]).

The exact number of bound states of the system for a given l value can be obtained by determining the number of zeros (other than at $r = 0$) in the regular solution to the radial Schrödinger equation with potential $V(r)$ and energy $E = 0$ (Bargmann[54]). This is

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usually done by step-by-step numerical integration on a computer.

Unfortunately, Gertler et al.[57] found that when m is the mass of the positron, $V(r)$ as given in eq 19 could support one bound state. Thus their attempt to prove that e^+H has no bound states failed.

Fortunately, Aronson et al.[58] were able to get around this difficulty. The ground state of e^+H is an S state. By making an adiabatic separation in which r_1, and *not* $\mathbf{r}_1$ as previously, is fixed, Aronson et al. were able to obtain a new adiabatic Hamiltonian, $\hat{H}'_{ad}$, having the following properties:

$$\langle\Psi|\hat{H}_{ad}|\Psi\rangle \leq \langle\Psi|\hat{H}'_{ad}|\Psi\rangle \tag{21}$$

$$\langle\Psi|\hat{H}'_{ad}|\Psi\rangle \leq \langle\Psi|\hat{H}_{int}|\Psi\rangle \tag{22}$$

where $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ is any allowed square-integrable function of S symmetry. In addition, $\hat{H}'_{ad}$ and $\hat{H}_{int}$ have the same continuum threshold, $-(1/2)m_2$. Thus if $\hat{H}'_{ad}$ has no bound states, this is also true for $\hat{H}_{int}$.

The potential $V'(r)$ associated with $\hat{H}'_{ad}$ is of the form

$$V'(r) = \frac{1}{r} + E'_0(r) - E_H^{(0)} \tag{23}$$

where $E'_0(r) \geq E_0(r)$. Aronson et al.[58] showed that it is extremely unlikely that $V'(r)$ can support a bound state and hence it is highly probable that no bound state of e^+H exists. This result is supported by information from scattering calculations (Humberston[59]). Aronson et al. showed further that it is highly probable that no bound state of e^+H exists for $m_1 < 1.46m_e$ and $m_2 = m_e$.

However, Aronson et al.[58] were unable to establish their conclusion rigorously. Armour[60] made their method of proof rigorous. Using the variational method and basis functions in terms of prolate spheroidal coordinates, he first of all calculated a very accurate wavefunction for the system described by $\hat{H}'_e$, the analogue of $\hat{H}_e$ in this adiabatic separation. He was able to calculate a good lower bound to $V'(r)$ using this wavefunction and the method of Temple[61] and Kato[62] and show that this lower bound, and hence $V'(r)$, could not support a bound state. In a later paper, Armour and Schrader[63] showed that if $m_1 = 1.51m_e$ and $m_2 = m_e$, no bound state of the e^+H system exists. To date this is the best lower bound on the critical positron mass required for binding.

So far we have assumed that the mass, m_3, of the proton in the e^+H system is infinite. In this case it is the ratio m_1/m_2 which determines whether or not a bound state exists. It follows that Armour's result[60] for the case $m_1 = m_2 = m_e$ shows that this Hamiltonian has no bound state for $m_1 = m_2$, whatever the value of m_2. It follows from this that if the system is to have a bound state when m_3 is finite and thus

$$\hat{H}_{int} = -\frac{1}{2\mu_{13}}\nabla_{\mathbf{r}_1}^2 - \frac{1}{2\mu_{23}}\nabla_{\mathbf{r}_2}^2 - \frac{1}{m_3}\nabla_{\mathbf{r}_1}\cdot\nabla_{\mathbf{r}_2} + \frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{r_{12}} \tag{24}$$

this must be due to the presence of the mass polarization term. As pointed out earlier, $e^-e^+e^-$ (and hence $e^+e^-e^+$) is known to have a bound state (Wheeler[2]). Its existence must be due to the large mass polarization term in this case.

This term can be taken into account with a method by Armour.[64] He was able to show that no bound state of $\hat{H}_{int}$ exists if the Hamiltonian

$$\hat{H}'_{int} = -\frac{1}{2m_1}\nabla_{\mathbf{r}_1}^2 - \frac{1}{2\mu_{23}}\nabla_{\mathbf{r}_2}^2 + \frac{Q}{r_1} - \frac{1}{r_2} - \frac{Q}{r_{13}} \tag{25}$$

where

$$Q = \frac{m_3 + m_2}{m_3 - m_2}$$

does not have a bound state. $\hat{H}'_{int}$ represents the internal motion, in the infinite proton mass approximation, of a system made up of a "positron" of the usual mass but with charge Q and an "electron" of mass μ_{23} and the usual charge.

As $\hat{H}'_{int}$ does not involve the mass polarization term, the method described earlier can be applied to it. In the case of e^+H,

$$Q = 1.0011 \quad \text{and} \quad \mu_{23} = 0.9995m_e$$

Thus it is not surprising that Armour[64] was able to show that no bound state of e^+H exists, even if the finite mass of the proton is taken into account.

Armour[65] also applied his method to $e^+e^-\mu^+$ for which

$$Q = 1.01 \quad \text{and} \quad \mu_2 = 0.995m_e$$

and to $e^+\mu^-p^+$ for which

$$Q = 1.254 \quad \text{and} \quad \mu_{23} = 186m_e$$

He was able to show that no bound states of either system exist.

The positions on the ternary diagram of the three unstable ions $e^+e^-p^+$, $e^+e^-\mu^+$, and $e^+\mu^-p^+$ considered above are all close to the left-hand side of the diagram and far away from the stable region as determined variationally by Poshusta.[22] They are thus of little help in determining a useful upper bound to the region of stability. However, we have seen that $2.20m_e$ and $1.51m_e$ are upper and lower bounds, respectively, to the critical mass at which a positron, an electron, and an infinitely massive proton would just form a bound state.[42,63] It follows from this that the intercept of the exact boundary of the region of stability on the left-hand side of the ternary diagram must lie between $x_1 = 0.31$ and $x_1 = 0.40$. There does not appear to be an analogous result giving bounds on its intercept with the base of the diagram.

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