Stability of the hydrogen and hydrogenlike molecules

Jean-Marc Richard

Institut des Sciences Nucléaires, 53, avenue des Martyrs, 38026 Grenoble, France

and European Centre for Theoretical Studies in Nuclear Physics and Related Areas, strada delle Tabarelle 286,

Villazzano, Trento, Italy

(Received 23 November 1993)

We present a simple proof of the stability of the hydrogen molecule $(M^+M^+m^-m^-)$. It does not rely on the proton-to-electron mass ratio M/m being very large, and actually holds for arbitrary values of M/m. Some asymmetric molecules of the type $(m_1^+m_2^+m_3^-m_4^-)$ are also stable. Possible applications to molecules containing antiparticles and to exotic hadrons in the quark model are briefly outlined.

PACS number(s): 31.15.+q, 36.10.-k

I. INTRODUCTION

The study of the hydrogen molecule is usually carried out within the framework of the Born-Oppenheimer approximation [1]. The effective potential between the two protons exhibits a deep pocket of attraction, and there is no doubt that stability survives quantum fluctuations and other corrections due to the proton mass being finite. A simple and rigorous derivation of the stability is, however, desirable, as well as a systematic study of other four-unit-charge systems.

A proof of the stability of the hydrogen molecule was briefly outlined in a recent communication [2]. It does not rely on the proton mass M being very large as compared to the electron mass m. It is actually based on a result obtained for the M = m case: Hylleraas and Ore [3] have shown in 1947 that the positronium molecule $(e^+e^+e^-e^-)$ is stable against dissociation into two positronium atoms. The stability of the hydrogen molecule, and more generally of any $(M^+M^+m^-m^-)$ configuration, can be proved using a rescaled version of the wave function of the positronium molecule.

If one aims at mathematical rigor, one can object that in the analysis of Refs. [2,3], it is implicitly assumed that the lowest threshold consists of two neutral atoms. It is also desirable to make a connection with the usual approach to hydrogen binding, based on the Born-Oppenheimer limit $M/m \to \infty$. In a recent letter [4], the question of the thresholds is seriously addressed, and an alternative variational wave function was proposed, which proves stability for $M \ge 0.144m$, and reduces to the standard Heitler-London wave function in the limit $M/m \to \infty$. A more detailed account of this work on the thresholds and on the stability for $M \gg m$ will be published elsewhere [5].

In the present paper, we explain how stability in the equal-mass case $(e^+e^+e^-e^-)$ implies stability for all hydrogenlike configurations $(M^+M^+m^-m^-)$. Moreover, from the calculated binding energy of $(e^+e^+e^-e^-)$ with respect to its threshold $(e^+e^-) + (e^+e^-)$, we predict a minimal extension of the stability region toward even more asymmetric configurations of the type $(m_1^+m_2^+m_3^-m_4^-).$

Perhaps the stability of the Coulombic molecule $(p\Sigma^+\Omega^-\Xi^-)$ with baryon number B = 4 and strangeness S = 4 will be thought as being of marginal interest. (For the zoology of charged leptons, mesons, and baryons, we refer to the Review of Particles Properties [6].) There is, however, a very general and fundamental concern about understanding why matter sometimes shows up in large compounds and sometimes splits into small clusters. We hope to better penetrate the mechanism of molecular binding by studying how it is sensitive to the masses of the constituents which are involved. Moreover, our approach to hydrogen binding allows for some generalizations. As briefly outlined in Sec. VIII, exotic molecules involving a mixture of matter and antimatter might well be stable, as long as annihilation is neglected. The stability problem also exists in other fields. In quark physics, only the minimal configurations have been seen so far, namely mesons made out of a quark and an antiquark, and baryons consisting of three quarks. We shall mention in Sec. IX that the patterns observed in molecular physics might provide some guidance in quark physics, or at least in simple quark models, to guess which flavor configurations are the most likely to host stable multiquarks.

II. THE STABILITY PROBLEM

Let us consider four elementary particles, with masses m_i , and unit electric charges $q_i = (+1, +1, -1, -1)$. There are obvious symmetries: an overall charge conjugaison, as well as $(1 \leftrightarrow 2)$ and $(3 \leftrightarrow 4)$ exchanges, leave the problem of stability invariant. So one can assume without loss of generality that

$$m_1 \ge m_2, \qquad m_3 \ge m_4, \tag{1}$$

and that the positive charges are on the average heavier than the negative ones, if there is any overall asymmetry.

In most cases, instability manifests itself by dissociation into two neutral atoms. For some values of the mass

3573

ratios, the lowest threshold consists of a three-body ion and a charge, for instance, $(m_1m_2m_3)^+ + m_4^-$: we know that $(m_1^+m_2^+m_3^-)$ is stable in a wide range of values of m_2/m_1 and m_3/m_1 [7,8]; in particular, every ion with $m_1 = m_2$ is stable [9]; moreover, if m_1 , m_2 , and m_3 are large, the binding energy of $(m_1m_2m_3)^+$ might well exceed (in absolute value) that of every other threshold. However, a molecule $(m_1^+m_2^+m_3^-m_4^-)$ would hardly decay into $(m_1m_2m_3)^+ + m_4^-$, since the long-range Coulomb attraction would keep the ion and the charge together. In other words, if the lowest threshold is made of a threebody ion and a charge, the stability of the four-body molecule is guaranteed. We shall come back to this point in Sec. VI.

The difficult task is thus to compare the four-body ground state to the thresholds consisting of two neutral atoms. Out of the two possible arrangements, (1,3) + (2,4) and (1,4) + (2,3), the former is more stable, if one assumes the mass ordering (1). This can be seen directly from the Bohr formula for the two-body energy, $E_2(m_i^+, m_j^-) = -1/(2\alpha_{ij})$, with $\alpha_{ij} = m_i^{-1} + m_j^{-1}$ being the inverse reduced mass. This is in fact a rather general result [10]. If v(r) is a universal potential (independent of the masses), the reduced two-body Hamiltonian $h = \alpha \mathbf{p}^2/2 + v(r)$ depends on the inverse reduced mass α linearly. Then the ground-state energy $E_2(\alpha)$ is a concave function of α [11], and if (1) is satisfied, $E_2(\alpha_{13}) + E_2(\alpha_{24}) \leq E_2(\alpha_{14}) + E_2(\alpha_{23})$.

Some states lying above the threshold are metastable, since their decay involves painful rearrangements and tunnelings. We shall not consider them.

One should also mention unnatural parity states. Imagine a molecule carrying orbital angular momentum and parity $J^P = 1^+$, besides the intrinsic spins and parities of its constituents. It cannot decay into two groundstate atoms $j^P = 0^+$ separated by an orbital momentum $\ell = 1$. Its actual threshold is made of a ground state (1S) and an orbital excitation (2P). We shall not consider this problem further, but simply mention that some of the general methods and results presented in this paper can be extended to unnatural-parity configurations.

III. THE EQUAL-MASS CASE

The stability of the positronium molecule was shown in 1947 by Hylleraas and Ore [6], who used an elegant variational method. They first got rid of the scale by noticing that if $\Psi(\mathbf{r}_i)$ is a trial wave function, with norm and expectation values of the kinetic and potential energies written as

$$n = \langle \Psi | \Psi \rangle, \quad t = \langle \Psi | T | \Psi \rangle, \quad v = \langle \Psi | V | \Psi \rangle, \quad (2)$$

then the best rescaling of the type $\phi = \Psi(\mathbf{r}_i/\lambda)$ yields a minimum

$$\widetilde{E} = -\frac{v^2}{4tn},\tag{3}$$

which corresponds to $\langle \phi | T | \phi \rangle = - \langle \phi | V | \phi \rangle / 2$, i.e., the same sharing of the kinetic and potential energies as for

the exact solution. This extension of the virial theorem to variational approximations is well known [12].

The frozen-scale wave function of Hylleraas and Ore contains a single parameter:

$$\Psi = \exp -\frac{1}{2}(r_{13} + r_{14} + r_{23} + r_{24}) \\ \times \cosh \frac{\beta}{2}(r_{13} - r_{14} - r_{23} + r_{24}).$$
(4)

Explicit integration leads to (a misprint in Ref. [3] is corrected below)

$$n = \frac{33}{16} + \frac{33 - 22\beta^2 + 5\beta^4}{16(1 - \beta^2)^3},$$
(5a)

$$t = \frac{21}{8} - \frac{3\beta^2}{2} + \frac{21 - 6\beta^2 + \beta^4}{8(1 - \beta^2)^3},$$
 (5b)

$$v = \frac{19}{6} + \frac{21 - 18\beta^2 + 5\beta^4}{4(1 - \beta^2)^3} - \frac{1}{(1 - \beta^2)^2} \left[1 - \frac{5\beta^2}{8} - \frac{1}{4\beta^4} + \frac{7}{8\beta^2} + \frac{(1 - \beta^2)^4}{4\beta^6} \ln \frac{1}{1 - \beta^2} \right],$$
(5c)

to be inserted in (2) and (3), leading to a minimum $\tilde{E} = -0.5042$ near $\beta^2 = 0.48$.

It is rather easy to generalize the calculation of Ref. [3] to a trial wave function of the type

$$\Psi = \sum_{i} c_{i} \exp -a_{i}(r_{13} + r_{14} + r_{23} + r_{24}) \\ \times \cosh b_{i}(r_{13} - r_{14} - r_{23} + r_{24}), \tag{6}$$

but one does not gain much [13]. As analyzed for instance, by Ho [14] and by the authors he quotes, some explicit r_{12} and r_{34} dependence is needed in the wave function to improve the accuracy. The last variational calculation [15] gives an energy one can express as

$$E(e^+e^+e^-e^-) = -(1+x_1)/2, \qquad x_1 = 0.03196,$$
 (7)

where x_1 represents the fraction of additional binding with respect to the threshold, which is $E_{\rm th} = -1/2$ in our units.

IV. FROM THE POSITRONIUM TO THE HYDROGEN MOLECULE

Once the stability of $(e^+e^+e^-e^-)$ is established, it is extremely simple to derive that of every $(M^+M^+m^-m^-)$ configuration [2,4]. Let us, indeed, rewrite the Hamiltonian as

$$H = H_S + H_A, \tag{8a}$$

$$H_{S} = \left(\frac{1}{4M} + \frac{1}{4m}\right) \left(\mathbf{p}_{1}^{2} + \mathbf{p}_{2}^{2} + \mathbf{p}_{3}^{2} + \mathbf{p}_{4}^{2}\right) + V, \quad (8b)$$

$$H_{A} = \left(\frac{1}{4M} - \frac{1}{4m}\right) \left(\mathbf{p}_{1}^{2} + \mathbf{p}_{2}^{2} - \mathbf{p}_{3}^{2} - \mathbf{p}_{4}^{2}\right), \qquad (8c)$$

where H_S is even under charge conjugaison, and H_A odd. One notices that H and H_S have the same dissociation threshold, namely, $-(M^{-1} + m^{-1})^{-1}$ in our units. Now, H_S is stable by simple rescaling of the positroniummolecule case, and the ground state of H is lower than that of H_S . This latter result comes from the variational principle, with the ground state of H_S , $\Psi(H_S)$, used as a trial wave function for H:

$$E(H) \le \langle \Psi(H_S) | H_S + H_A | \Psi(H_S) \rangle = E(H_S)$$
(9)

since $\langle \Psi(H_S) | H_A | \Psi(H_S) \rangle$ vanishes, by symmetry considerations.

It is amazing that every exotic molecule with the same structure as hydrogen is stable. An example is $D^+D^+\Omega^-\Omega^-$, with charm C = 2 and strangeness S = -6.

Previously, Abdel-Raouf [16] and Rebane [17] stressed the regularity of the binding energy as a function of the mass ratio M/m, but missed the fact that stability in the positronium case implies stability for other $(M^+M^+m^-m^-)$ configurations.

If one fixes, for instance, the scale by m = 1, one can study the lowest energy E of $(M^+M^+m^-m^-)$ as a function of s = 1/M, or equivalently the fraction x(s) defined as the positronium case as

$$E(M^+M^+m^-m^-) = -\frac{1+x(s)}{1+s},$$
 (10)

 $E_{\rm th} = -1/(1+s)$ being the threshold energy. The fraction x(s) takes the values $x_1 = 0.0303$ in the positronium case (s = 1), and $x_0 = 0.1745$ for s = 0, the limit of hydrogen with infinitely massive protons. The values are taken from the compilation by Rebane [17]. This means the inequality (9), $E(H) < E(H_{\rm S})$, is actually observed.

Since s enters the Hamiltonian linearly, E(s) is a concave function of s [11]. On can also combine convexity and scaling and deduce that -1/E(s) is also concave, and this provides a stronger constraint [11]. The concavity of -1/E leads to an upper bound on x(s) for intermediate configurations

$$1 + x(s) \le \frac{1+s}{2} \left[\frac{s}{1+x_1} + \frac{1-s}{2(1+x_0)} \right]^{-1}.$$
 (11)

V. ASYMMETRIC MOLECULES

Let us go by steps toward $(m_1^+m_2^+m_3^-m_4^-)$, which denotes the most general case. Consider first a different arrangement of only two masses, $(M^+m^+M^-m^-)$. We saw that it is stable for M = m. In the case of a large asymmetry $M \gg m$, it seems to become unstable: the hydrogen-antihydrogen system, for instance, hardly survives its decay into $(p\bar{p}) + (e^+e^-)$.

A minimal domain of stability around M = m can be derived from the variational principle. One can fix the scale by setting $M^{-1} = 1 - y$ and $m^{-1} = 1 + y$. Then

$$H(M^{+}m^{+}M^{-}m^{-}) = \frac{1}{2} \left(\mathbf{p}_{1}^{2} + \mathbf{p}_{2}^{2} + \mathbf{p}_{3}^{2} + \mathbf{p}_{4}^{2} \right)$$
$$+ V + \frac{y}{2} \left(-\mathbf{p}_{1}^{2} + \mathbf{p}_{2}^{2} - \mathbf{p}_{3}^{2} + \mathbf{p}_{4}^{2} \right).$$
(12)

The reasoning is the same as in Sec. IV. The last term, antisymmetric under simultaneous $(1 \leftrightarrow 2)$ and $(3 \leftrightarrow 4)$ exchanges, lowers the ground-state energy. Then from Eq. (7),

$$E(y) \le E_{\rm th}(0)(1+x_1).$$
 (13)

Meanwhile the threshold becomes

$$E_{\rm th}(y) = -\frac{1}{4(1-y)} - \frac{1}{4(1+y)} = \frac{E_{\rm th}(0)}{1-y^2}.$$
 (14)

Thus stability remains at least as long as $y^2 \leq 1 - (1 + x_1)^{-1}$, i.e., for

$$0.70 \le \frac{M}{m} \le 1.43$$
 . (15)

Now, if one starts from $(M^+m^+M^-m^-)$, and introduce four different masses m_i such that

$$m_1 \ge m_2, \quad m_3 \ge m_4, \quad m_1^{-1} + m_3^{-1} = 2M^{-1},$$

 $m_2^{-1} + m_4^{-1} = 2m^{-1},$ (16)

then one can rewrite the Hamiltonian as

$$H(m_1^+ m_2^+ m_3^- m_4^-) = H(M^+ m^+ M^- m^-) + \frac{1}{4}(m_1^{-1} - m_3^{-1})(\mathbf{p}_1^2 - \mathbf{p}_3^2) + \frac{1}{4}(m_2^{-1} - m_4^{-1})(\mathbf{p}_2^2 - \mathbf{p}_4^2), \quad (17)$$

and, again, the two last terms cannot do anything but lower the ground-state energy, while the threshold does not change. Hence stability is improved.

For instance, $(\overline{\Omega^-}\Sigma^+\Xi^-\overline{p})$ is stable, as long as strong interactions are neglected, since the constituent masses are here 1.67, 1.20, 1.32 and 0.94 GeV/ c^2 , which fulfill (15) and (16). We are not too surprised to learn that the positronium hydride $(pe^+e^-e^-)$ is stable, by a small margin [18]: it corresponds to M/m = 2, not too far outside our minimal range (15), and benefits from the large asymmetry between particles 1 and 3.

The role of symmetries should be emphasized. Consider, for instance, the stability of $(1^+, 1^+, 1^-, m^-)$, whose threshold is

$$E_{\rm th}(m) = E_{\rm th}(1) \frac{1+\delta/4}{1+\delta/2},$$
 (18)

where $\delta = m^{-1} - 1$ measures the departure from the symmetric case of the positronium molecule. One can first split the Hamiltonian into

$$H(m) = H(1) + \frac{\delta}{2}\mathbf{p}_4^2,$$
 (19)

and say that the ground state should lie below the first-

order estimate. The expectation value of \mathbf{p}_4^2 is easily estimated from the virial theorem and the symmetries of the unperturbed wave function. Then

$$E(m) \leq E(1)\left(1-\frac{\delta}{4}\right),$$
 (20)

leading to a sufficient condition for stability

$$\frac{1+\delta/4}{(1-\delta/4)(1+\delta/2)} = 1 + \frac{\delta^2}{8} + \dots \le 1+x_1.$$
 (21)

If one instead splits the Hamiltonian into pieces of wellidentified behavior under permutations

$$H = \left[\left(1 + \frac{\delta}{4} \right) \sum \mathbf{p}_i^2 + V \right] + \frac{\delta}{8} \left(-\mathbf{p}_1^2 + \mathbf{p}_2^2 - \mathbf{p}_3^2 + \mathbf{p}_4^2 \right) + \frac{\delta}{4} \left(-\mathbf{p}_2^2 + \mathbf{p}_4^2 \right), \qquad (22)$$

one gets

$$E(m) \le E(1) \frac{1}{1+\delta/4},$$
 (23)

corresponding to a wider range of stability

$$\frac{(1+\delta/4)^2}{1+\delta/2} = 1 + \frac{\delta^2}{16} + \dots \le 1 + x_1.$$
 (24)

VI. VERY ASYMMETRIC MOLECULES

We already mentioned that some configurations are qualitatively different from the positronium molecule, since their lowest threshold does not consist of two neutral atoms. These configurations cannot be studied by starting from $(e^+e^+e^-e^-)$, and implementing more and more asymmetry.

Consider, for instance, the molecule $(\Lambda_c^+ \Lambda_c^+ \Omega^- e^-)$, with charmed hyperons, or any similar case where three particles are much heavier than the fourth one, and form a stable ion. Its stability results from the $(\Lambda_c^+ \Lambda_c^+ \Omega^-)$ ion lying below its dissociation threshold into an atom and a charge, as is the case for every $m_1^+m_2^+m_3^-$ ion with $m_1 = m_2$ [9,7]. The electron is bound around this ion, but the electronic energy is negligible.

We expect interesting properties in the transition region where a threshold consisting of a three-body ion and a charge becomes equal to the lowest threshold made of two neutral atoms. The competing thresholds are likely to generate some attraction in the whole four-body system, and make it stable. This particular situation deserves some specific investigations.

VII. TENTATIVE GRAPHICAL SUMMARY

Thanks to the scaling properties of the Coulomb interaction, the study of a system of N given charges requires only (N-1) independent variables to scan all possible mass distributions.

In the case of three unit charges $q_i = \pm (-1, 1, 1)$, one could introduce two independent mass ratios. It was however found more convenient to use three barycentric coordinates α_i , with $0 \le \alpha_i \le 1$, and a normalization $\sum \alpha_i = 1$. Each case corresponds to a point inside an equilateral triangle, in which a stability frontier separates the stability from the instability areas. One can choose the masses as barycentric coordinates, as in Fig. 1. The inverse masses of Fig. 2 prove more suited for the mathematical analysis of the observed convex behavior of the frontier [8].

The generalization to N = 4 charges corresponds the inner volume of a regular tetrahedron, so that the stability frontier keeps the symmetries of the problem. We shall summarize our results and our guesses both with the masses m_i as variables $(\sum m_i = 1)$, or the inverse masses $\alpha_i \propto m_i^{-1}$ $(\sum \alpha_i = 1)$, restricting ourselves to very schematic drawings of the unfolded tetrahedrons. Future theoretical and numerical works will hopefully make it possible to determine the frontier more accurately.

Consider first the representation in terms of the masses, in a regular tetrahedron (ABCD) of unit height, so that $\sum m_i = 1$, with m_1 being the distance to the face (BCD), etc. This corresponds to Fig. 3.

The summit A, stands for the masses $m_i = (1, 0, 0, 0)$,

FIG. 1. Graphical representation of the stability domain for three-unit charges $q_i = \pm (-1, 1, 1)$ with normalized masses m_i , $\sum m_i = 1$. The stability domain includes the symmetry axis (dotted line) where $m_2 = m_3$.







FIG. 2. Graphical representation of the stability domain for three-unit charges $q_i = \pm (-1, 1, 1)$ with normalized inverse masses $\alpha_i = 1/m_i$, $\sum \alpha_i = 1$. The stability domain includes the symmetry axis (dotted line) where $\alpha_2 = \alpha_3$.

i.e., the limit of a positronium hybride $(pe^+e^-e^-)$ with an infinitely massive proton. It is stable, at least for $m_2 = m_3 = m_4$ [18]. This means the stability domain reaches A, at least along the symmetry axis. A similar situation is, of course, observed near B, C, and D. To our knowledge, there is no result available on how stability survives when the light masses m_2, m_3 , and m_4 are different, in particular, for $m_1 \gg m_3 \sim m_4 \gg m_2$, corresponding to the trace of the stability border on the face (ACD). For $m_1 \gg m_3 = m_4 \gg m_2$, we have a heavy stable (1,3,4) ion which attracts the charge m_2 , a stable situation according to the discussion in Sec. VI.

The middle between A and C corresponds to masses $m_i \propto (1,0,1,0)$, i.e., a configuration $(pe^+\bar{p}e^-)$, which seems unstable. We suspect there is no stability at all along AC, and similarly along AD, BC, and BD. This guess has, of course, to be checked.

On the other hand, the middle between A and B describes the hydrogen molecule (ppe^-e^-) with $m_i = (1,1,0,0)$. This is a region of confortable stability. We guess that stability holds all the way along AB. There is no doubt $(pp'e^-e^-)$ is stable as long as both $m(p) \gg m(e)$ and $m(p') \gg m(e)$, since the Born-



FIG. 3. Schematic picture of the stability domain for four unit charges $q_i = (-1, -1, 1, 1)$. The stability frontier is shown by its trace on the unfolded faces of the tetrahedron (ABCD) of normalized masses m_i , $\sum m_i = 1$.

Oppenheimer approximation holds in such a case. Stability should remain, in our opinion, for $m(p) \gg m(e)$ and $m(p') \gtrsim m(e)$, as long as the equality $m_3 = m_4$ is kept. This, indeed, suffices to make the two thresholds (1,3)+(2,4) and (1,4)+(2,3) degenerate, and again, it is a general, though empirical, observation that competing thresholds often generate attraction; one could also say that the (pe^-) and $(p'e^-)$ atoms have comparable Bohr radii, and their overlap might lead to some favorable exchange forces between them.

The face (BDC) corresponds to $m_1 = 0$. As discussed in Sec. VI, the stability domain is generally dictated by the stability of the three-body system $(m_2^+m_3^-m_4^-)$, which is described in Fig. 1. Exceptions are found near the edges of (BCD), where we have more than one light particle. The situation is, of course, identical on the other faces.

Consider now the tetrahedron (ABCD) with normalized inverse distances, in Fig. 4. The summit A cor-



FIG. 4. Schematic picture of the stability domain for four unit charges $q_i = (-1, -1, 1, 1)$. The stability frontier is shown by its trace on the unfolded faces of the tetrahedron (ABCD) of inverse masses $\alpha_i = 1/m_i$, with normalization $\sum \alpha_i = 1$. The trace of the stability domain in the section (bcd) below the summit A looks like the 3-body domain of Fig. 2.

responds to the $(e^+p\bar{p}\bar{p})$, when one goes to A along the symmetry axis. This is a stable protonium ion surronded by an electron, i.e., a stable four-body configuration. The shape of the stability domain near A is more precisely seen on a cross-section (bcd) parallel to (BCD) and close to A: the trace on (bcd) looks exactly as the stability plot of Fig. 2, because we are in the regime of Sec. VI where one of the masses is much lighter than of the others.

The sides AB and CD correspond to inverse masses (0, 0, x, 1 - x), with $0 \le x \le 1$, i.e., to configurations (ppee') with $m(e) \ll m(p)$ and $m(e') \ll m(p)$, but the ratio of m(e) to m(e') arbitrary. We believe they are stable.

The sides AC, AD, BC, and BD have inverse masses of the type (x, 0, 1 - x, 0), i.e. $(e^+pe'\bar{p})$, for which dissociation seems likely to occur spontaneously.

These speculations suggest the topology schematically drawn in Fig. 4. Note that with these variables, a face such as (BCD) describes situations of the type $[pe^+(e')^-(e'')^-]$, where (with obvious notations) m, m', and m'' are much lighter than M. It is stable for m = m' = m'', with little excess binding [18]. We thus expect the stability band to be rather narrow near the center of (BCD).

VIII. LARGER MOLECULES

An obvious extension of the present study consists of considering $N = N_+ + N_- > 4$ unit charges. The problem is, in general, rather complex, due, in particular, to the proliferation of competing thresholds, but one can retain from the study in the N = 4 case that simplifications occur when very different masses are involved.

Consider, for instance, N = 5, with masses and charges $(M^+M^+M^-m^-m^-)$, and $M \gg m$. The heavy core $(M^+M^+M^-)$ is stable, by simple rescaling of the positronium-ion case $(e^+e^-e^-)$. It acts as a localized positive charge, and should bind two electrons, with a wave function very similar to that of the familiar $H^{-}(pe^{-}e^{-})$ ion. A similar reasoning was applied to molecular complexes involving muons and electrons [19]. If $(M^+M^+M^-m^-m^-)$ is stable for large M/m, a cooled antiproton could be trapped in a hydrogen molecule, before annihilating. According to the current analysis [20], when a \bar{p} is captured in hydrogen, it quickly expels the electrons by Auger emission; a protonium atom $(p\bar{p})$ is formed in a highly excited state, and it rapidly decays toward states of low orbital momentum, where its annihilates. Recently some events with delayed annihilation have been reported, stimulating some theoretical studies [21,22]: some metastable states with an antiproton, a nucleus, and some electrons might be formed in rare occasions. The above $(pp\bar{p}e^-e^-)$ compound is another new possibility.

Similarly, for N = 6, and $N_+ = N_- = 3$, the state $(ppe^+\bar{p}e^-e^-)$ is probably stable, due to the combined stability of the $(pp\bar{p})$ ion and of the positronium hybride $(pe^+e^-e^-)$.

The symmetric case of N = 6, $(m^+m^+m^+m^-m^-m^-)$, is much more delicate. Stability seems excluded for actual electrons, due to the Pauli principle, but one can address the question for pions, π^+ and π^- , which are bosons. The lowest threshold is $(m^+m^+m^-m^-) + (m^+m^-)$, so one has to show that the lowest energy Edecreases faster than -N, already for small N. For large N, a behavior $E \propto -N^{7/5}$ has been identified [23].

IX. APPLICATIONS TO HADRON SPECTROSCOPY

A simple, but phenomenologically successful, description of the hadron spectrum is the nonrelativistic quark model. Mesons are quark-antiquark bound states, and baryons consist of three quarks. An interesting property is *flavor independence*. At first approximation, i.e., without spin forces and relativistic corrections, the potential is the same whatever quarks, u, d, s, c, or b, are bound together. This is reminiscent from atomic physics, where the very same $-r^{-1}$ potential acts in hydrogen, positronium, protonium, etc.

In quark models with flavor independence, one expects some of patterns observed in atomic physics, those which are due to the universality of the potential, and independent of its particular Coulombic shape. For instance, the convexity property mentioned in Sec. II for the two-body energies is satisfied, and the inequality

$$Q\overline{Q} + q\bar{q} \le 2Q\bar{q} \tag{25}$$

has indeed been noticed [10], and observed in the experimental spectrum [6].

We have seen that among the four-body molecules, $(ppe^{-}e^{-})$ was the most stable. It is not surprising that explicit four-quark calculations [2,24] have led to the prediction that the exotic configuration $(QQ\bar{q}\bar{q})$ becomes stable if the mass ratio m(Q)/m(q) is large enough, whereas the equal-mass case $QQ\bar{Q}\bar{Q}$ seems unbound. In this field, one calls "exotic" a state whose quantum numbers, in particular flavor, cannot be matched by ordinary quark-antiquark or three-quark structures. Other multiquarks are predicted on the basis of spin-dependent forces, but this is out of the scope of this paper. It is hoped that double-charm, or charm-and-beauty spectroscopy will reveal some good surprises.

X. CONCLUSIONS

Let us summarize our results about four-unit-charge systems, which bear a sharply decreasing degree of rigor.

We first recalled the proof by Hylleraas and Ore of the stability of the positronium molecule [3]. It can be supplemented by a rigorous study of the ordering of the various possible thresholds [4,5].

Once the stability of $(e^+e^+e^-e^-)$ is established, that of the hydrogenlike molecules $(M^+M^+m^-m^-)$ follows rigorously [2,4]. This is essentially a consequence of the variational principle.

Now, one can prove a minimal extension of the stability domain toward other directions like $(M^+m^+M^-m^-)$ or $(m_1^+m_2^+m_3^-m_4^-)$, if one takes for granted a nonrigorous input, namely, the actual binding energy of $(e^+e^+e^-e^-)$, which results from numerical variational calculations.

The above results are far from covering all possible configurations. To picture how the stability domain could look like, we have substituted some missing results by simple guesses, which have to be checked. For instance, we feel that the asymmetric hydrogen molecule $(pp'e^-e^-)$ remains stable whatever mass is given to p', as long as $m(p) \gg m(e)$. We have also assumed without proof that $(pe^+\bar{p}'e^-)$ immediately breaks into $(p\bar{p}') + (e^+e^-)$, except near the limit $m(p') \rightarrow m(e)$.

We also presented some plausible but nonrigorous extensions to larger molecules and to multiquark systems in the quark model.

In spite of its weaknesses, this study illustrates once

more how quantum binding energies have a simple and well-controlled behavior when one varies the constituent masses without changing the potential. It is hoped it will stimulate some interest for the investigations which remain to be done.

ACKNOWLEDGMENTS

I would like to thank D. M. Brink for useful comments and discussions. The hospitality provided by ECT^{*} at Trento is gratefully acknowledged. The Institut des Sciences Nucléaires is supported by Université Joseph Fourier and CNRS-IN2P3.

- See, for instance, L.I. Schiff, Quantum Mechanics, 3rd ed. (McGraw-Hill, New York, 1968); P.J.E. Peables, Quantum Mechanics (Princeton University Press, Princeton, 1992).
- [2] J.-M. Richard, in *Quark Cluster Dynamics*, Proceedings of the Bad Honnef Workshop, 1992, edited by K. Goeke, P. Kroll, and H.R. Petry (Springer-Verlag, Berlin, 1993).
- [3] E.A. Hylleraas and A. Ore, Phys. Rev. 71, 493 (1947).
- [4] J.-M. Richard, J. Fröhlich, G.M. Graf, and M. Seifert, Phys. Rev. Lett. 71, 1332 (1993).
- [5] M. Seifert, U. of Zürich Diplomarbeit (1993) (unpublished).
- [6] Particle Data Group, Review of Particle Properties, special issue of Phys. Rev. D 45 Pt. II (1992); 46, 5210(E) (1992).
- [7] E.A.G. Armour and W. Byers Brown, Acc. Chem. Res. 26, 168 (1993).
- [8] A. Martin, J.-M. Richard, and T.T. Wu, Phys. Rev. A 46, 3697 (1992).
- [9] R.N. Hill, J. Math. Phys. 18, 2316 (1977).
- [10] R. Bertlmann and A. Martin, Nucl. Phys. B168, 11 (1980).
- [11] W. Thirring, Quantum Mechanics of Atoms and Molecules, A Course in Mathematical Physics Vol. 3 (Springer-Verlag, New York, 1983).
- [12] E.A. Hylleraas, Z. Phys. 54, 347 (1929); V. Fock, *ibid.* 63, 855 (1930).
- [13] A. Ore, Phys. Rev. 71, 913 (1947).

- [14] Y.K. Ho, Phys. Rev. A33, 3584 (1986).
- [15] P.M. Kozlowski and L. Adamowicz, Phys. Rev. A 48, 1903 (1993).
- [16] M.A. Abdel-Raouf, in Few-Body Problems in Particle, Nuclear, Atomic, and Molecular Physics, Proceedings of the European Few-Body Systems Conference, Fontevraud, France, 1987, edited by J.-L. Ballot and M. Fabre de la Ripelle (Springer-Verlag, Wien, 1987).
- [17] T.K. Rebane, Yad. Fiz. 50, 746 (1989) [Sov. J. Nucl. Phys. 50, 466 (1989)].
- [18] D.M. Schrader, F.M. Jacobsen, N.P. Frandsen, and U. Mikkelsen, Phys. Rev. Lett. 69, 57 (1992); 69, 2880(E) (1992), and references therein.
- [19] M.P. Faifman et al., Z. Phys. D 2, 79 (1986).
- [20] G. Reifenröther and E. Klempt, Nucl. Phys. A 503, 885 (1989); E. Klempt (unpublished).
- [21] T. Yamazaki, Zeit. Phys. A 341, 233 (1992); T. Yamazaki et al., Nature 361, 238 (1993).
- [22] K. Richter *et al.*, Phys. Rev. Lett. **66**, 149 (1991), and references therein.
- [23] J.G. Conlon, in Proceedings of the 9th International Congress on Mathematical Physics, Swansea, Wales, 1988, edited by B. Simon et al. (Hilger, Bristol, 1989).
- [24] J.-P. Ader, J.-M. Richard, and P. Taxil, Phys. Rev. D 25 195 (1982); S. Zouzou et al., Z. Phys. C 30, 457 (1986);
 L. Heller and J.A. Tjon, Phys. Rev. D 32, 755 (1985); 35, 969 (1987); J. Carlson, L. Heller and J.A. Tjon, *ibid.* 37, 744 (1988); H.J. Lipkin, Phys. Lett. B 172, 242 (1986).



FIG. 3. Schematic picture of the stability domain for four unit charges $q_i = (-1, -1, 1, 1)$. The stability frontier is shown by its trace on the unfolded faces of the tetrahedron (ABCD) of normalized masses m_i , $\sum m_i = 1$.



FIG. 4. Schematic picture of the stability domain for four unit charges $q_i = (-1, -1, 1, 1)$. The stability frontier is shown by its trace on the unfolded faces of the tetrahedron (ABCD) of inverse masses $\alpha_i = 1/m_i$, with normalization $\sum \alpha_i = 1$. The trace of the stability domain in the section (bcd) below the summit A looks like the 3-body domain of Fig. 2.