Proof of Stability of the Hydrogen Molecule

J.-M. Richard
Institut des Sciences Nucléaires, Université Joseph Fourier, 53 avenue des Martyrs, Grenoble, France

J. Fröhlich, G.-M. Graf, and M. Seifert
Theoretical Physics, Eidgenössische Technische Hochschule Zürich-Hönggerberg, Zürich, Switzerland
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We sketch two rigorous proofs of the stability of the hydrogen molecule in quantum mechanics. The first one is based on an extrapolation of variational estimates of the ground state energy of a positronium molecule to arbitrary mass ratios. The second one is an extension of Heitler-London theory to nuclei of finite mass.

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The stability of the hydrogen molecule H_2 (ppe^-e^-) plays an important role in our understanding of chemical binding and thus deserves a mathematically precise analysis. It appears that, within the usual formalism of nonrelativistic quantum mechanics, a rigorous proof of the fact that the system (ppe^-e^-) has bound states, i.e., that H_2 is stable, is not available in the literature, at least to our knowledge.

In this Letter, we sketch two somewhat complementary proofs of the stability of H_2. The first proof starts from a four-body system consisting of two particles of charge $+1$ and two particles of charge -1, all of which have the same mass, i.e., from a system corresponding to a positronium molecule, the stability of which has been essentially established by Hylleraas and Ore [1], up to a subtlety concerning the threshold of the continuous spectrum.

An elementary variational argument can then be used to extrapolate upper bounds on the ground state energy of systems where the positively charged particles have mass M and the negatively charged ones have mass m to arbitrary ratios m/M. These bounds will prove binding, for any value of m/M, including the case of H_2.

The second proof is inspired by the Heitler-London theory of binding in the Born-Oppenheimer limit, corresponding to $m/M \to 0$, and extends that theory to an interval $0 \leq m/M \leq 0.144$. For small values of m/M it yields better bounds than the first proof.

Details of these results, including a study of stability as a function of the masses of the constituent particles will be presented in forthcoming papers by Richard [2] and Seifert [3].

Throughout this paper, we shall employ units in which the reduced mass and the ground state energy of the actual hydrogen atom are $Mm/(M+m) = 1$ and $E_0(pe^-) = -1$, and we restrict our analysis to Coulomb systems, except for a remark in the conclusions.

To determine the nature of binding in the H_2 molecule, one has first to understand the ordering of the threshold energies that appear when the system (ppe^-e^-) or (dpe^-e^-) is decomposed into two or more noninteracting clusters. We only consider the system (ppe^-e^-), but the arguments for a system like (dpe^-e^-) are similar.

The minimal energy of a decomposition of (ppe^-e^-) into four noninteracting clusters is obviously $E_4 = 0$, the one of a decomposition into three noninteracting clusters, $(pe^-)(p)(e^-)$, is $E_3 = E_0(pe^-) = -1$. The third and fourth decompositions are into the clusters $(pe^-e^-)(p)$ and $(e^-pp)(e^-)$. Their energies are given by $E_0(pe^-e^-)$ and $E_0(e^-pp)$, i.e., the lowest energy $E^{(3)}(\lambda)$ of

$$H(\lambda) = \lambda \mathbf{p}_1^2 + (1-\lambda)\left(\mathbf{p}_2^2 + \mathbf{p}_3^2\right) + \frac{2}{r_{23}} - \frac{2}{r_{12}} - \frac{2}{r_{13}} \quad (1)$$

for $\lambda = m/(M+m)$ and $\lambda = M/(M+m)$, respectively. Here $r_{ij} = |\mathbf{x}_i - \mathbf{x}_j|$, and M and m denote the masses of the proton and the electron. By the variational principle, we have

$$E^{(3)}(\lambda) \geq \lambda E^{(3)}(1) + (1-\lambda)E^{(3)}(0) \quad (2)$$

for $0 \leq \lambda \leq 1$.

Consider first the case $\lambda = 0$. It corresponds to a modified H^- ion with an infinitely massive proton, and electrons whose mass is rescaled to 1, in our units. Hill [4] has shown that this system has exactly one bound state with the electrons in a spin-singlet state. However, the ground state energy $E^{(3)}(0)$ is not known exactly. As a result of

$$H(0) \geq H_0 = \left(\mathbf{p}_2^2 - \frac{2}{r_{12}}\right) + \left(\mathbf{p}_3^2 - \frac{2}{r_{13}}\right), \quad (3)$$

we find $E^{(3)}(0) \geq -2$. This can be improved by taking into account the electronic repulsion $V_{23} = 2/r_{23}$ and using the projection method [5]. We have $H(0) = H_0 + V_{23}$, with V_{23} positive, and thus

$$E^{(0)}(0) \geq E_0(H_0) + \left\langle \psi_0, V_{23}^{-1}\psi_0 \right\rangle^{-1}, \quad (4)$$

where ψ_0 is the ground state of H_0, with energy $E_0(H_0) = -2$. Evaluating the right hand side of this inequality yields the bound

$$E^{(0)}(0) > -\frac{5}{4}, \quad (5)$$

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in our units. The case $\lambda = 1$ corresponds to (ppe^-) with infinitely massive protons, i.e., a limiting case of hydrogen ion $H_2{}^+$. The stability of the $H_2{}^+$ ion has been established by Hill [4], but the exact value of $E_0\,(ppe^-)$ is not known. Thus we must prove a suitable lower bound on $E_0\,(ppe^-)$. This can be accomplished by using the Born-Oppenheimer approximation, which is exact here, and the so-called criterion of local energy [5]. Let H_R denote the Hamiltonian of the system with the protons separated by a distance R, and a single quantum mechanical electron. The Perron-Frobenius theorem guarantees that H_R has a unique ground state $\varphi_R(\mathbf{x})$ which is a positive function of the electron position $\mathbf{x}$. The corresponding ground state energy is denoted by E_R. Let $\varphi(\mathbf{x})$ be a positive function of $\mathbf{x}$, and define $E_R(\mathbf{x}) := \varphi(\mathbf{x})^{-1}\,(H_R\varphi)\,(\mathbf{x})$. Then

$$\inf_{\mathbf{x}} E_R(\mathbf{x}) \leq E_R \leq \sup_{\mathbf{x}} E_R(\mathbf{x}), \tag{6}$$

as one easily shows. Thus

$$E_0\,(ppe^-) > \min_R E_R \geq \min_R[\inf_{\mathbf{x}} E_R(\mathbf{x})]\,. \tag{7}$$

Choosing $\varphi(\mathbf{x})$ to be proportional to $\exp(-\alpha\mu)\cosh(\beta\nu)$, with $\mu = (r_1 + r_2)/R$ and $\nu = (r_1 - r_2)/R$, where r_i is the distance between the electron and the ith proton, one obtains, after a tedious calculation (using elliptic coordinates) and for an optimal choice of the constants α and β, that $E^{(3)}(1) > -1.6225$. The inequality (2) then implies $E^{(3)}(\lambda) > -2$ for all $0 \leq \lambda \leq 1$. In particular, we have

$$E_0(pe^-e^-), E_0(e^-pp) > 2E_0\,(pe^-) = -2 \tag{8}$$

for all mass ratios, and thus the lowest threshold always corresponds to the decompostion into two neutral atoms.

The Hunziker–Van Winter–Zhislin (HVZ) theorem [6] now tells us that the continuous spectrum of the Hamiltonian $H^{(4)}$ of the four-body system (ppe^-e^-) is the interval $[E_c, \infty)$, with $E_c = 2E_0\,(pe^-)$, for all m/M. In particular, when m/M is given its physical value then

$$\sigma_{\text{continuous}}(H^{(4)}) = [-2, \infty). \tag{9}$$

Thus, to prove that the system (ppe^-e^-) has bound states, it suffices to construct a variational wave function, ψ, with the property that

$$\langle\psi, H^{(4)}\psi\rangle < -2. \tag{10}$$

We shall sketch two somewhat complementary methods to construct a ψ such that (10) holds. The first method to prove (10) starts from a beautiful argument of Hylleraas and Ore [1] suggesting that the positronium molecule $(e^+e^+e^-e^-)$ is bound. We make use of their results in a way that has been outlined briefly in [7]. They use the simple variational wave function $\psi\,(\lambda\mathbf{x}_i)$, where

$$\psi\,(\mathbf{x}_i) = \exp -\frac{1}{2}\,(r_{13} + r_{14} + r_{23} + r_{24}) \times \cosh\frac{\beta}{2}\,(r_{13} - r_{14} - r_{23} + r_{24})\,. \tag{11}$$

The scale parameter λ is determined by the virial theorem (which holds for variational bounds [8]), and the variational energy $E_0(\beta)$ can be calculated explicitly [1,2]. As a result one finds that

$$E_0\,(e^+e^+e^-e^-) \leq \min_\beta E_0(\beta) \simeq 2.0168E_0\,(e^+e^-)\,, \tag{12}$$

and the minimum is reached near $\beta^2 = 0.48$. The threshold of the continuous spectrum in $(e^+e^+e^-e^-)$ is twice the ground state energy of positronium, i.e.,

$$E_c = 2E_0\,(e^+e^-)\,. \tag{13}$$

Next, we rewrite the Hamiltonian $H^{(4)}$ of the hydrogen molecule as

$$H^{(4)} = H_S + H_A, \tag{14}$$

where

$$\begin{aligned} H_S &= \left(\frac{1}{2M} + \frac{1}{2m}\right)(\mathbf{p}_1^2 + \mathbf{p}_2^2 + \mathbf{p}_3^2 + \mathbf{p}_4^2) + V, \\ V &= \frac{2}{r_{12}} + \frac{2}{r_{34}} - \frac{2}{r_{13}} - \frac{2}{r_{14}} - \frac{2}{r_{23}} - \frac{2}{r_{24}}, \\ H_A &= \left(\frac{1}{2M} - \frac{1}{2m}\right)(\mathbf{p}_1^2 + \mathbf{p}_2^2 - \mathbf{p}_3^2 - \mathbf{p}_4^2)\,, \end{aligned} \tag{15}$$

where H_S is even under charge conjugation and H_A is odd; see [7]. The symmetric Hamiltonian H_S corresponds to a rescaled version of the positronium molecule, with the constituent mass m replaced by $2Mm/(M+m)$. We notice that the minimal energies in the spectra of $H^{(4)}$ and of H_S for two infinitely separated neutral atoms are identical. We know that this is the lowest threshold for any value of m/M. It then follows immediately from (12) that the lowest energy in the spectrum of H_S satisfies

$$E_0(H_S) \leq 2.0168E_0\,(pe^-)\,, \tag{16}$$

which is strictly smaller than -2 if m/M is given its physical value. Next, we note that

$$E_0(H^{(4)}) < \langle\psi_0^S, (H_S + H_A)\psi_0^S\rangle\,, \tag{17}$$

where ψ_0^S is a normalized wave function symmetric under charge conjugation, like the one used by Hylleraas and Ore, and such that $\langle\psi_0^S, H_S\psi_0^S\rangle < E_0(H_S) + \epsilon$, for some $\epsilon > 0$ which can be chosen arbitrarily small. Since H_A is odd under charge conjugation, $\langle\psi_0^S, H_A\psi_0^S\rangle = 0$. Hence it follows that

$$E_0(H^{(4)}) < E_0(H_S) \leq 2.0168E_0\,(pe^-) \tag{18}$$

which, by (10), proves that (ppe^-e^-) is bound, for any value of m/M, in particular when m/M is given its physical value. The inequality $E_0\,(H^{(4)}) < E_0(H_S)$ is reflected nicely in actual binding energies which grow from 3% for the positronium molecule to 17% for the hydrogen molecule, according to the estimates reported in [9]. Previously, Abdel-Raouf [10] and Rebane [9] stressed the regularity of the binding energy as a function of m/M,

but missed the fact that the bound (12) for $m = M$ implies binding for m/M small enough. Let us finally sketch how the results on the thresholds can be combined with an improved version of Heitler-London theory to prove binding for the hydrogen molecule. We remove the center-of-mass motion, and introduce the distances $\mathbf{Y}$ between the two nuclei, and $\mathbf{y}_i$ $(i = 1, 2)$ between their middle and the electrons, so that the Hamiltonian reads, in suitable units, as

$$H^{(4)} = -\frac{1}{M}\Delta_Y - \frac{1}{2\mu}\Delta_{y_1} - \frac{1}{2\mu}\Delta_{y_2} - \frac{1}{2M}\nabla_{y_1}\cdot\nabla_{y_2} - 2\sum_{\substack{i=1\\ \epsilon=\pm 1}}^{2}\frac{1}{|\mathbf{y}_i + \epsilon\mathbf{Y}/2|} + \frac{2}{|\mathbf{Y}|} + \frac{2}{|\mathbf{y}_1 - \mathbf{y}_2|}, \quad (19)$$

with $\mu = 2Mm/(2M + m)$. Within the Born-Oppenheimer approximation, suitable ansatz wave functions are the ones of Heitler and London given by

$$\varphi_\pm(\mathbf{Y}, \mathbf{y}_1, \mathbf{y}_2) = C_\pm[f(|\mathbf{y}_1 - \mathbf{Y}/2|)f(|\mathbf{y}_2 + \mathbf{Y}/2|) \pm f(|\mathbf{y}_1 + \mathbf{Y}/2|)f(|\mathbf{y}_2 - \mathbf{Y}/2|)] \quad (20)$$

with + corresponding to spin singlet and − corresponding to spin triplet for the electrons, and $f(r) = \text{const} \times \exp(-2\mu r)$. The orbital ground state wave function of the hydrogen molecule is symmetric in the electron positions. This motivates us to use the following variational wave function:

$$\psi(\mathbf{Y}, \mathbf{y}_1, \mathbf{y}_2) = C(\beta)|\mathbf{Y}|e^{-\beta|\mathbf{Y}|}\varphi_+(\mathbf{Y}, \mathbf{y}_1, \mathbf{y}_2), \quad (21)$$

where $C(\beta)$ is a constant chosen such that $\langle\psi, \psi\rangle = 1$. After very tedious calculations and lengthy estimates carried out in [3], one finds that, for an optimal choice of β,

$$\langle\psi, H^{(4)}\psi\rangle < -2.082, \quad (22)$$

which proves (10) and hence establishes the result that (ppe^-e^-) is bound. As shown in [3], this method proves stability and provides an estimate of the binding energy for $0 \leq (m/M) \leq 0.144$. Our methods can be extended, in principle, to systems of three and four particles interacting through "universal" (mass- and flavor-independent) two-body potentials. Binding will be strongest in systems of four particles with masses (M, M, m, m) in the limiting regime when $M \gg m$. Simple quark models have flavor-independent potentials, and one thus is led to predict stability of exotic mesons $(QQ\bar{q}\bar{q})$ with two units of heavy flavor [7].

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