# PROOF OF STABILITY OF THE HYDROGEN MOLECULE

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**Abstract**

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 groundstate 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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## 1. Introduction

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 non-relativistic 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 $H_2$. [Details will appear elsewhere [1], [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 (3), 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 groundstate energy of systems where the positively charged particles have mass $M$ and the negatively charged ones have mass $m$ to arbitrary ratios $\frac{m}{M}$. These bounds will prove binding, as long as $\frac{m}{M} \leq 0.6$, 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 J.-M.R. [1] and M.S. [2].

Throughout this paper, we shall employ units in which the groundstate energy of the actual hydrogen atom is $-1$, and we restrict our analysis to Coulomb systems, (except for a remark in the conclusions).

## 2. The thresholds in the spectrum of $H_2$

To determine the nature of binding in the $H_2$ molecule, one has to understand the ordering of the threshold energies that appear when the system $(ppe^-e^-)$ or $(dpe^-e^-)$, is decomposed into two or more non-interacting 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 non-interacting clusters is obviously $E_4 = 0$, the one of a decomposition into three non-interacting clusters,

$(pe^-)(p)(e^-)$, is $E_3 = E_0(pe^-)$, where $E_0(pe^-)$ is the groundstate energy of the hydrogen molecule which, in our units, is $E_0(pe^-) = -1$.

The third decomposition is into the clusters $(pe^-e^-)(p)$. The minimal energy of the resulting system is $E_2 = E_0(pe^-e^-)$, where $E_0(pe^-e^-)$ is the groundstate energy of the system $(pe^-e^-)$. Hill [4] has shown that this system has exactly one bound state with the electrons in a spin-singlet, the groundstate of the $H^-$ ion. However, the groundstate energy $E_0(pe^-e^-)$ of the $H^-$ ion is not known exactly. We shall need a somewhat accurate lower bound on $E_0(pe^-e^-)$. The easiest such bound is obtained by neglecting the Coulomb interaction between the electrons and the kinetic energy of the proton. The lower bound is then twice the groundstate energy of the hydrogen atom where the reduced mass $\mu$ is replaced by the electron mass $m > \mu$, i.e., $E_0(pe^-e^-) > -2 - \text{const.}10^{-3}$, with const. $\approx \frac{1}{2}$. This bound is very bad and is insufficient for our purposes. It must be improved by taking into account the electronic repulsion. This can be done by using the projection method [5]. By $H_0$ we denote the Hamiltonian of the system $(pe^-e^-)$, but where the mass $M$ of the positively charged particle, the proton, is set to $\infty$ and *without* the Coulomb repulsion $V$, between the electrons. Let $H' = H_0 + V$, and let $H^{(3)}$ denote the true Hamiltonian of of system $(pe^-e^-)$. Denoting the groundstate energy of a Hamiltonian $H$ by $E_0(H)$, we then have

$$E_0\left(H^{(3)}\right) > E_0(H') \geq E_0(H_0) + \langle \psi_0, V^{-1}\psi_0 \rangle^{-1}, \tag{1}$$

where $\psi_0$ is the groundstate of $H_0$. Evaluating the right hand side of this inequality yields the bound

$$E_0\left(H^{(3)}\right) > -\frac{5}{4}\left(1 + \frac{m}{M}\right), \tag{2}$$

in our units. Thus

$$E_0\left(H^{(3)}\right) > -2, \quad \text{for} \quad \frac{m}{M} \leq \frac{3}{5}, \tag{3}$$

and

$$E_0\left(H^{(3)}\right) > -1.2507 \tag{4}$$

if $\frac{m}{M}$ is given its physical value.

The fourth decomposition of the system $(ppe^-e^-)$ into non-interacting clusters is $(ppe^-)(e^-)$. Its lowest energy is given by $E_2' = E_0(pe^-e^-)$, the groundstate energy of the hydrogen ion $H_2^+$. Again, 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 and the so-called criterion of local energy [5]. Setting the proton mass $M$ to $\infty$ we obtain a two-center problem, with the protons separated by a distance $R$, for a single quantum mechanical electron. Let $H_R$ denote the Hamiltonian of this system. The Perron-Frobenius theorem guarantees that $H_R$ has a unique groundstate $\varphi_R(\overrightarrow{x})$ which is a positive function of the electron position $\overrightarrow{x}$. The corresponding groundstate energy is denoted by $E_R$. Let $\varphi(\overrightarrow{x})$ be a positive function of $\overrightarrow{x}$, and define $E_R(\overrightarrow{x}) := \varphi(\overrightarrow{x})^{-1}\,(H_R\varphi)(\overrightarrow{x})$. Then

$$\inf_{\overrightarrow{x}} E_R(\overrightarrow{x}) \le E_R \le \sup_{\overrightarrow{x}} E_R(\overrightarrow{x}), \tag{5}$$

as one easily shows. Thus

$$E_0\,(ppe^-) > \min_R E_R \ge \min_R \left( \inf_{\overrightarrow{x}} E_R(\overrightarrow{x}) \right) \tag{6}$$

Choosing $\varphi(\overrightarrow{x})$ to be proportional to $\exp(-\alpha\mu)\cosh(\beta\nu)$, with $\mu = \frac{r_1 + r_2}{R}$ and $\nu = \frac{r_1 - r_2}{R}$, where $r_i$ is the distance between the electron and the $i^{\text{th}}$ proton, one obtains, after a tedious calculation (using elliptic coordinates) and for an optimal choice of the constants $\alpha$ and $\beta$, that

$$E_0\,(ppe^-) > -2, \quad \text{for} \quad \frac{m}{M} \le 0.605 \tag{7}$$

and

$$E_0\,(ppe^-) > -1.623 \tag{8}$$

if $\frac{m}{M}$ is given its physical value. Details of the proof will appear in [2]. Our bounds suggest that $E_2 = E_0\,(pe^-e^-) > E_2' = E_0\,(ppe^-)$, and this can presumably be proven by refining the estimates in [2].

Finally, we consider the decompositon of the system $(ppe^-e^-)$ into two non-interacting hydrogen atoms $(pe^-)(pe^-)$. The lowest energy, $E_2''$, of the resulting system is, of course,

$$E_2'' = 2E_0\,(pe^-) = -2 \tag{9}$$

We define

$$E_c = \min\,\{E_4, E_3, E_2, E_2', E_2''\} \tag{10}$$

Since $0 = E_4 > E_3 > E_2, E_2' > E_2'' = -2$, we have that $E_c = -2$. The 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 $\frac{m}{M} \leq 0.6$. In particular, when $\frac{m}{M}$ is given its physical value then

$$\sigma_{\text{continuous}}\left(H^{(4)}\right) = [-2, \infty). \tag{11}$$

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

$$\left\langle \psi, H^{(4)}\psi \right\rangle < -2. \tag{12}$$

We shall sketch two somewhat complementary methods to construct a $\psi$ such that (12) holds.

## 3. Variational upper bounds on the groundstate energy of $H_2$.

The first method to prove (12) starts from a beautiful argument of Hylleraas and Ore [3] 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 $\psi\left(\left(\lambda \overrightarrow{x}_i\right)\right)$, where

$$\psi\left(\left(\lambda \overrightarrow{x}_i\right)\right) = \exp -\frac{1}{2}\left(r_{13} + r_{14} + r_{23} + r_{24}\right)\cosh\frac{\beta}{2}\left(r_{13} - r_{14} - r_{23} + r_{24}\right),$$

with $r_{ij} = \left|\overrightarrow{x}_i - \overrightarrow{x}_j\right|$. The scale parmeter $\lambda$ is determined by the virial theorem (which holds for variational bounds [8]), and the variational energy $E_0(\beta)$ can be calculated explicitly [1], [3]. As a result one finds that

$$E_0\left(e^+e^+e^-e^-\right) \leq \min_{\beta} E_0(\beta) \simeq -2.0168 E_0\left(e^+e^-\right), \tag{14}$$

and the minimum is reached near $\beta^2 = 0.50$. The threshold of the continuous spectrum in $(e^+e^+e^-e^-)$ is expected to be twice the groundstate energy of positronium, i.e.,

$$E_c = 2E_0\left(e^+e^-\right) \tag{15}$$

but the equality between $E_c$ and $2E_0\left(e^+e^-\right)$ has not been rigorously established for the positronium molecule, yet. However, we neither need this equality in the following arguments, nor is it needed to prove binding for $(e^+e^+e^-e^-)$.

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

$$H^{(4)} = H_S + H_A, \tag{16}$$

where

$$\begin{cases} H_S & = \left(\frac{1}{4M} + \frac{1}{4m}\right)\left(\vec{p}_1^{\,2} + \vec{p}_2^{\,2} + \vec{p}_3^{\,2} + \vec{p}_4^{\,2}\right) + V \\ H_A & = \left(\frac{1}{4M} - \frac{1}{4m}\right)\left(\vec{p}_1^{\,2} + \vec{p}_2^{\,2} - \vec{p}_3^{\,2} - \vec{p}_4^{\,2}\right), \end{cases} \tag{17}$$

where $H_S$ is even under charge conjugation and $H_A$ is odd ; see [7]. We now notice that the minimal energies in the spectra of $H^{(4)}$ and of $H_S$ for two infinitely separated hydrogen atoms are identical. When $\frac{m}{M} \leq 0.6$ we know from Sect. 2 that this is the lowest threshold. It then follows immediately from (14) that the lowest energy in the spectrum of $H_S$ satisfies

$$E_0(H_S) \leq 2.0168 E_0\left(pe^-\right) \tag{18}$$

which is strictly smaller than $-2$ if $\frac{m}{M}$ is given its physical value. Next, we note that

$$E_0\left(H^{(4)}\right) < \left\langle \psi_0^S, H_S + H_A)\psi_0^S \right\rangle, \tag{19}$$

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

$$E_0\left(H^{(4)}\right) < E_0(H_S) \leq 2.0168 E_0\left(pe^-\right) \tag{20}$$

which, by (12), proves that $(ppe^-e^-)$ is bound, provided $\frac{m}{M} < 0.6$, in particular when $\frac{m}{M}$ is given its physical value.

The inequality $E_0\left(H^{(4)}\right) < E_0(H_S)$ 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 and Rebane [10] stressed the regularity of the binding energy as a function of $\frac{m}{M}$, but missed the fact that the bound (14) for $m = M$ implies binding for $\frac{m}{M}$ small enough.

Let us finally sketch how the results in Sect. 2 can be combined with an improved version of Heitler-London theory to prove binding for the hydrogen molecule. In nuclear center-of-mass coordinates, the Hamiltonian for the hydrogen molecule is given (in suitable units) by

$$H^{(4)} = -\frac{1}{M}\Delta_Y - \frac{1}{2\widetilde{\mu}}\Delta_{y_1} - \frac{1}{2\widetilde{\mu}}\Delta_{y_2} - \frac{1}{2M}\overrightarrow{\nabla}_{y_1} \cdot \overrightarrow{\nabla}_{y_2}$$

$$-2 \sum_{\substack{i=1 \\ \epsilon=\pm 1}}^{2} \frac{1}{|\overrightarrow{y}_i + \frac{\epsilon}{2}\overrightarrow{Y}|} + \frac{2}{|\overrightarrow{Y}|} + \frac{2}{|\overrightarrow{y}_1 - \overrightarrow{y}_2|}, \tag{21}$$

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

$$\varphi_\pm(\overrightarrow{Y}, \overrightarrow{y}_1, \overrightarrow{y}_2) = C_\pm \left[ f\left(|\overrightarrow{y}_1 - \frac{1}{2}\overrightarrow{Y}|\right) f\left(|\overrightarrow{y}_2 + \frac{1}{2}\overrightarrow{Y}|\right)\right.$$

$$\left. \pm f\left(|\overrightarrow{y}_1 + \frac{1}{2}\overrightarrow{Y}|\right) f\left(|\overrightarrow{y}_2 - \frac{1}{2}\overrightarrow{Y}|\right)\right] \tag{22}$$

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

$$\psi\left(\overrightarrow{Y}, \overrightarrow{y}_1, \overrightarrow{y}_2\right) = C(\beta)|\overrightarrow{Y}|e^{-\beta|\overrightarrow{Y}|}\varphi_+\left(\overrightarrow{Y}, \overrightarrow{y}_1, \overrightarrow{y}_2\right), \tag{23}$$

where $C(\beta)$ is a constant chosen such that $\langle\psi, \psi\rangle = 1$.

After very tedious calculations and lengthy estimates carried out in [2], one finds that, for an optimal choice of $\beta$,

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

which proves (12) and hence establishes the result that $(ppe^-e^-)$ is bound.

## 4. Conclusions and outlook.

We have sketched two variational proofs of the stability of the hydrogen molecule. Both proofs are based on the analysis of thresholds in the spectrum of $(ppe^-e^-)$ sketched in Sect. 2 and worked out in detail in [2]. The first proof is based on the variational wave function of Hylleraas and Ore for the positronium molecule ($m = M$) and extrapolation in $\frac{m}{M}$, while the second proof is inspired by the Heitler-London theory in the Born-Oppenheimer approximation $\left(\frac{m}{M} = 0\right)$.

Details of these proofs and extensions of our results to more general three- and four-body systems will appear in forthcoming papers by J.-M.R. [1] and M.S. [2].

We also remark that there is a variant of our methods which yields a very simple proof of binding $(ppe^-e^-)$, for arbitrary values of $\frac{m}{M}$, but does not provide quantitative estimates on binding energies.

Our methods can be extended, in principle, to systems of three and four particles interacting through "universal" (mass- and flavour-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 flavour-independent potentials [11], and one thus is led to predict stability of exotic mesons $(Q, Q, \overline{q}, \overline{q})$ with two units of heavy flavour [7].

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