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The stability of S-states of unit-charge Coulomb three-body systems: From H− to H2+

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High accuracy non-relativistic quantum chemical calculations of the ground state energies and wavefunctions of symmetric three-particle Coulomb systems of the form \(\{m_1^+, m_2^+, m_3^+\}\), \(m_1 = m_2\), are calculated using an efficient and effective series solution method in a triple orthogonal Laguerre basis set. These energies are used to determine an accurate lower bound to the stability zone of unit-charge three-particle Coulomb systems using an expression for the width of the stability band in terms of \(g\), the fractional additional binding due to a third particle. The results are presented in the form of a reciprocal mass fraction ternary diagram and the energies used to derive a parameterised function \(g(a_3)\), where \(a_3 = m_3^{-1} / (m_1^{-1} + m_2^{-1} + m_3^{-1})\) is the reciprocal mass of the uniquely charged particle. It is found that the function is not minimal at \(a_3 = 0\) which corresponds to \(\infty H^-\) nor is it minimal at the positronium negative ion (Ps−) the system with the least absolute energetic gain by association with a third particle; the function \(g(a_3)\) is minimal at \(m_3/m_3 = 0.49\), and a possible physical interpretation in terms of the transition from atomic-like to molecular-like is provided.

I. INTRODUCTION

Quantum chemistry is dominated by methods based on two major approximations: the Born-Oppenheimer (B-O) approximation and the orbital approximation (within Kohn-Sham theory or wavefunction-based theory). While for most applications such methods are perfectly adequate, being able to provide both qualitative and quantitative insight into the structure, bonding, reactivity, and spectroscopy of systems of experimental interest and often to the level of "chemical accuracy," there are systems for which these "standard" quantum chemical techniques are unsatisfactory. Thus, for example, the B-O approximation fails to correctly account for the occurrence of conical intersections. Furthermore, there is a need to ensure methods remain competitive with the increasingly accurate experimental work, for example, on molecular spectra. There are several examples in the recent literature that advance these approximations, to name just a few, see the work by Cederbaum, Sutcliffe, regarding going beyond the standard B-O approximation and the work by Gill et al. attempting to provide a "universally accurate and efficient approach" to electron correlation.

Here, we present the results of high accuracy, non-relativistic, quantum chemical calculations of the energy levels and wavefunctions of three-particle systems. Such systems hold a unique position, as they represent the simplest problem that encompasses both atomic and molecular ions. Usually an assumption about the structure of a particular system – atomic or molecular – is made a priori and then the Schrödinger equation solved accordingly; however, when the masses of the particles are similar the justification for the clamped nucleus or the Born-Oppenheimer approximation is not appropriate, and as highlighted by Mátúš et al. this qualitatively different description of "atomic" and "molecular" systems does not follow from a purely mathematical discussion. In this paper, we unify the treatment of atomic and molecular systems of the form \(\{m_1^+, m_2^+, m_3^+\}\) by treating all particle masses as finite and using a Laguerre-based wavefunction with two nonlinear parameters. This allows us to move smoothly from atomic-like to molecular-like systems. The results also provide highly accurate data for electron-correlated atomic systems (such as H−) and non-B-O molecular systems (such as H2+). The former is relevant, for example, for those involved in density function theory developments.

An additional reason for the importance of three-particle systems is that there are many three-particle Coulomb systems, including those involving elementary particles, such as positrons, muons, protons, and their anti-matter counterparts, that are of topical interest to both the chemistry and physics communities. For example, \(d^+ t^+ \mu^-\) is known to catalyse nuclear fusion at room temperature and the recent discrepancy between determinations of the proton radius using muonic hydrogen spectroscopy involved consideration of weakly bound three-body systems such as \((p \mu e)^-\) and \((pp \mu)^+.\) Furthermore, the muonium negative ion \((e^- e^- \mu^+\) has been observed as an impurity during muon spin resonance spectroscopy used to probe hydrogen impurities in semiconductors and a range of materials. Particularly relevant to such studies is an understanding of the stability of three-body Coulomb system, i.e., the conditions under which a bound state is formed. This matter is specifically addressed in the present work.

Several investigators have attempted to predict the stability of Coulombic three-particle systems based on their mass ratios. Whereas some have attempted to use mass ratios to predict the stability of specific exotic systems such as...
p+e+e−,14,15 and p+μ−e−,11,20 others have focussed on developing a general understanding of the role that mass ratios play in the binding energy of Coulombic three-particle systems.13,16–18,23 Stability of a system in this work is defined as the existence of at least one bound state below the lowest continuum threshold.22

Here, we consider three-body systems of the form \{m1, m2, m3\} interacting via a Coulomb potential but without recourse to the clamped-nucleus or Born-Oppenheimer approximation. In the case of three-body atoms or ions, there is a unique choice of a body-fixed coordinate system for states with angular momentum J = 0, namely, in which the three particles define a plane and the translation-free internal coordinates are chosen to be the inter-particle distances.23 It is a property of Coulomb interaction that all masses can be scaled, and given that the inverse masses occur linearly in the Hamiltonian, Martin et al.13 have shown that all possible cases can be plotted on a ternary diagram, as shown in Figure 1(a), in terms of the normalised reciprocal mass fraction coordinates,

\[
a_i = \frac{1}{m_i + 1/m_1 + 1/m_2}, \quad i = 1, 2, 3
\]

such that

\[
a_1 + a_2 + a_3 = 1.
\]

Hill24 proved that all symmetric (m1 = m2) systems are stable against dissociation into a two-particle system and a free particle, but no such formal proof exists for atoms and molecules of the general form \{m1, m2, m3\}, where m1 ≠ m2 and, in fact, such systems are only stable within a certain range of particle mass.19 Martin et al.13 estimated the lower bound of this stability region by deriving a function, δ(a3), defined in Eq. (3), for the horizontal width of the stability band, Figure 1(b), in terms of g(a3), where g is the fraction of additional binding gained by association with a third particle in symmetric systems and a3 is the reciprocal mass of the uniquely charged particle

\[
\delta(a_3) \geq \frac{2}{\sqrt{3}} \frac{g(a_3)}{1 + g(a_3)}(1 + a_3).
\]

The purpose of this paper is twofold. First, we describe an improvement in the rate of energy convergence compared to previous calculations by Cox et al.,23,25 on inclusion of additional nonlinear parameters in the wavefunction. The optimum wavefunction is used to calculate accurate energies, E0, for a wide range of unit-charge, symmetric, three-body systems of the form \{m1, m2, m3\}, involving the particles listed in Table I. There are 36 distinct, symmetric, singly charged ions ranging from atomic to molecular (72 including the anti-particle counterparts which, by charge inversion invariance, have the same energy as those presented, e.g., E(p+e−) = E(p−e+)). Additionally, some hypothetical mass systems are calculated to ensure an even distribution of data points along the symmetric axis of the reciprocal mass fraction

![Figure 1](https://example.com/figure1.png)

**FIG. 1.** (a) Reciprocal mass fractions as coordinates on a ternary diagram and (b) the width of the stability band δ(a3) about the m1 = m2 symmetry axis (dashed line) for a given value of a3.

### Table I. Masses of the particles (and anti-particles) used in this work.

<table>
<thead>
<tr>
<th>Particle</th>
<th>Symbol</th>
<th>Mass (m_{particle}/m_{e})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron</td>
<td>e−</td>
<td>1</td>
</tr>
<tr>
<td>Muon</td>
<td>μ−</td>
<td>206.768 284 3</td>
</tr>
<tr>
<td>Tauon</td>
<td>τ−</td>
<td>3477.15</td>
</tr>
<tr>
<td>Proton</td>
<td>p+/H+</td>
<td>1836.152 672 45</td>
</tr>
<tr>
<td>Deuteron</td>
<td>d+/D+</td>
<td>3670.482 965 2</td>
</tr>
<tr>
<td>Triton</td>
<td>t+/T+</td>
<td>5496.921 526 7</td>
</tr>
</tbody>
</table>

These are to be compared with the values (in units of m_e) used in previous calculations: m_e = 206.768 262, Refs. 30, 33, 39, and 40, m_p = 206.768 275, Ref. 41, m_μ = 1836.152 701, Refs. 30, 33, and 42, m_τ = 1836.152 667 5, Ref. 39, m_d = 3670.483 014, Refs. 30, 33, and 43, and m_t = 5495.688 449, Ref. 41. Note, the masses of Frollov et al. have been converted from MeV/c^2 using the conversion m_e = 0.510998 928 MeV/c^2 and use the most recent experimental values; his m_e and m_μ values are in complete agreement with those used in the present work.
ternary diagram. Second, accurate values of the fractional additional binding $g$ are calculated using these $E_0$ values. The expression of Martin et al.\textsuperscript{13} for the width of the stability band (3) is used to determine an accurate lower bound to the stability zone of three-particle Coulomb systems, and the results are presented on a ternary diagram.\textsuperscript{13,22} Additionally, we present a functional fit of $g(\alpha)$. It is found that the mass ratio corresponding to the minimum in the function $g$ falls neatly in the range predicted by Mátyus et al.\textsuperscript{6} as the point at which molecular structure emerges in three-particle systems.

II. METHOD

The non-relativistic Schrödinger equation for the S-states of $\{m_1^2 m_2^2 m_3^2\}$ three-body systems is solved using the method described by Cox et al.\textsuperscript{23} In brief, the centre of mass motion is separated off and the internal coordinates are chosen as the inter-particle distances $r_1$, $r_2$, and $r_3$ which are, respectively, the 3-1, 3-2, and 1-2 inter-particle coordinates. The problem is then recast in perimetric coordinates\textsuperscript{26} defined as $z_i = r_j + r_k - r_i$, where $i, j, k$ denote cyclic permutation of 1, 2, and 3. Perimetric coordinates have the great advantage of being independent over their range from 0 to $\infty$ unlike the interparticle coordinates, which are connected by the triangular condition and thus have dependent domains. The resulting Schrödinger equation is solved using a series solution method by expanding the wavefunction in a triple orthogonal set of Laguerre functions\textsuperscript{27} in scaled perimetric coordinates

$$\psi(z_1, z_2, z_3) = e^{-\frac{1}{2} \alpha z_1 - \beta z_2 + \gamma z_3} \times \sum_{l,m,n=0}^{\infty} A(l,m,n) L_l(\alpha z_1) L_m(\beta z_2) L_n(\gamma z_3).$$

(4)

This results in a 57-term recursion relation between the coefficients, which is used to form a sparse secular determinant that is solved in truncated form to give the eigenvalues as a function of basis set size $N$.

Initially, as in previous work,\textsuperscript{25} the energy $E$ is removed from the Schrödinger equation by the relation

$$E = -K \varepsilon^2$$

(5)

and the nonlinear scale parameter $K$ is used variationally to improve convergence compared to the work of Pekeris\textsuperscript{27} who took $K = 1$. Setting $\alpha = \beta = \varepsilon$ and $\gamma = \alpha + \beta$ reduces the exponent in the wave function (4) to

$$(\alpha z_1 + \beta z_2 + \gamma z_3) = 2\varepsilon (r_1 + r_2) = \left(\frac{2}{\sqrt{K}}\right) \sqrt{-E}(r_1 + r_2).$$

When $K = 1$ this, in principle, is an exact form as it contains the correct asymptotic behaviour of the solution of the Schrödinger equation for two-electron atoms and ions at large $r_1$ and $r_2$.\textsuperscript{28} Although this works very well for atomic-like systems (with one heavy mass)\textsuperscript{23,28} and systems where all masses are similar (e.g., $\text{Ps}^-$)\textsuperscript{29} convergence for molecule-like systems (with two heavy masses) is very slow. Arias de Saavedra et al.\textsuperscript{30} have addressed this problem by ensuring an explicit dependence on $r_{12} (= r_3)$ in the exponential behaviour at large $r$, but do not include the energy parameter in their definition of the scaled perimetric coordinates. This explicit dependence on $r_3$ is achieved by relaxing the constraint $\alpha + \beta = \gamma$, i.e., $\alpha(=\beta)$ and $\gamma$ are varied independently. However, if the constraint $\alpha = \beta$ is also relaxed, then for symmetric systems with fermionic exchange the useful quasi-orthogonal character of the wavefunction is lost. Therefore, in this work which involves such systems, the condition $\alpha = \beta$ was imposed, and then either $\gamma = 2\varepsilon$ or no constraint was put on $\gamma$; for non-symmetric systems, i.e., non-identical particles, the variation of all three nonlinear parameters has also been implemented.

The nonlinear variational parameters were optimised using the conjugate gradient method in order to minimise the energy.\textsuperscript{31} However, for non-atomic systems with two nonlinear parameters ($\alpha, \varepsilon$) it was necessary to first perform a scan of the parameters due to the potential for multiple minima. When the calculation included the energy parameter $\varepsilon$ in the coordinates, and the electron was not the lightest mass, it was necessary either to scale the energy parameter by the mass of the lightest particle directly or to set the mass of the lightest particle to 1 (e.g., use muonic units). The masses for all the systems considered were taken from CODATA\textsuperscript{32} and are provided in Table I.

III. RESULTS

A. Energy convergence

Table II shows the nature of the basis sets with one and two nonlinear parameters and the effect of including the energy parameter $\varepsilon$ in the coordinates for $\text{H}^- (e^- e^+ p^+)$, $\text{Mu}^- (e^- e^- \mu^+)$, $\mu \text{H}^- (\mu^- \mu^- p^+)$, $\text{Ps}^- (e^- e^- e^+)$, $\mu \text{D}_2^+ (d^+ d^- \mu^-)$, $\mu \text{D}_2^+ (\mu^- \mu^+ e^-)$, $\text{H}_2^+ (p^+ p^- e^+)$, and $\text{D}_2^+ (d^+ d^- e^-)$. These were chosen as their mass ratios ($m_1/m_3$) vary from $5.446 \times 10^{-4}$ to $3.670 \times 10^3$. The masses for all the particles are included from the beginning in each calculation. This is highly advantageous as the mass-polarisation effects, for example, are automatically included and thus determined to a precision limited only by that of the physical constants. However, it does mean that any redetermination of the fundamental constants changes the precision of the energy obtained suggesting that energies should be recalculated with the new values. In this work, the latest CODATA values are used.\textsuperscript{32} In Table II, numbers reported in the literature that go beyond the precision of the masses used in this work are given in italics (and truncated).

As observed previously,\textsuperscript{25,29,30,33} the increase in the rate of convergence for atomic systems and for exotic two-electron systems ($\text{Ps}^-$ and $\text{Mu}^+$) is insignificant when a second nonlinear variational parameter is included. However, for systems with molecular character (such as $\text{H}_2^+$) the second nonlinear parameter is vital for reasonable convergence. This is due to the importance of having an adequate description of the interparticle distribution between the two heavier particles. Even then, the molecular-type systems (such as $\text{H}_2^+$ and $\text{D}_2^+$) converge more slowly than the atomic systems. For all, even the atomic systems, inclusion of the energy parameter in the description of the asymptotic behaviour is of no particular benefit. In the work that follows, a methodology that is suitable for
a range of symmetric, possibly unknown, systems is required and so the remainder of the data presented was obtained using a wave function with two nonlinear variational parameters, as this methodology was suitable for both atomic- and molecular-type systems.

The least accurate mass value used is known to 6 significant figures (s.f.), see Table I, thus all energies are converged and presented to at least 6 s.f. Typically, this level of convergence was achieved using either a 1078-term or a 1925-term wave function with two nonlinear variational parameters. In general, a full scan of the parameters followed by an optimisation at the minimum was performed at $N = 1078$ and/or $N = 1925$ followed by an optimisation at $N = 2856$ to determine the level of convergence.

### B. Stability criteria

The ground state energy of a wide-range of symmetric systems of the form $\{m_1^2, m_2^2, m_3^2\}$ were calculated in a series ranging from $\{(m_1 = m_2) \gg (m_3 = 1)\}$ to $\{(m_3 \gg (m_1 = m_2 = 1)\}$. For consistency, the charges on each particle were set as $\{m_1^2, m_2^2, m_3^2\}$, although reversing the charges would produce the same $E_0$ due to charge inversion invariance. The calculated energies for all the systems considered are given in Table III. To determine the stability of three-body systems, the lowest energy threshold is considered. In the case of three unit charges $\{m_1^2, m_2^2, m_3^2\}$, if we assume that $m_1 \geq m_2$, then the system will break up into $\{m_1^2, m_3^2\}$ (as the heavier bound pair will have a greater energy due to the dependence on reduced mass) and an isolated particle $m_2^2$ at rest at infinity. Therefore, the threshold energy of the three-particle system coincides with the ground-state energy of the two-body atom, which is simply the ground state energy of the hydrogen-like atom consisting of particles 1 and 3, i.e.,

$$E_{th} = E(m_1, m_3) = -\frac{1}{2} \frac{m_1 m_3}{2m_1 + m_3}. \quad (6)$$

Thus, the stability limit depends only on the ratio of the masses, and not their absolute values, and in this work given that $m_1 = m_2$, it depends only on $m_1/m_3$. Following the work of Martin et al., the stability of each system is measured in terms of $g$ a dimensionless ratio of the ground state energy of the three-body system ($E_0$) and the threshold energy ($E_{th}$):

$$g = \frac{E_0 - E_{th}}{E_{th}}. \quad (7)$$

### C. The function $g(a_3)$

A plot of $g$ against $a_3$ for a range of symmetric systems yields the graph depicted in Figure 2(a). Particularly interesting is that $g(a_3)$ does not decrease monotonically to $a_3 = 0$ corresponding to $\infty H^{-}$, but contains a minimum. Based on the data in Table III, this minimum is estimated to occur at $a_3 \approx 0.2$ which corresponds to the system $(p, p, d)^3$, with a mass ratio of $\approx 0.5$. To investigate this further, the data points listed in Table III and seven additional points having $a_3$ values between the data points $(\tau, \tau, \tau)^3$ and $(p, p, t)^3$ in increments of 0.01, were fitted to a functional form, and the function differentiated to determine the minimum as accurately as possible.

Previously, Martin et al. described $g(a_3)$ as having a square-root behaviour near $a_3 = 1$. By simply adding a
Taking this expansion to fifth order \((n = 5)\) results in an excellent fit with a \(R^2\) value of 0.999999980, Figure 2(b). The optimised values for this fit are: \(c_0 = 0.588 641 277, c_1 = 0.326 670 402, c_2 = 0.383 300 517, c_3 = 2.048 690 70, c_4 = 12.366 541 0, c_5 = 46.866 686 5, c_6 = 110.492 237, c_7 = 162.933 845, c_8 = 146.384 326, c_9 = 73.345 924 6, and \(c_{10} = 15.745 569 2\). Differentiating the function \(g(a_3)\) to determine the minimum provides the symmetric system that has
the least fractional binding energy gained by association with a third particle. However, the minimum is sensitive to the functional form and so additional data points were calculated about the minimum to estimate the accuracy. Based on this analysis, and comparing with alternative functional forms, the minimum is estimated to occur at $a_3 = 0.197 \pm 0.001$, corresponding to the system $(m_1 = m_2 = 1, m_3 = 2.04 \pm 0.01)$ which has a mass ratio of $m_1/m_3 = 0.491 \pm 0.003$.

### D. The stability band width $\delta$

Using the $g$ values directly, or from the parameterised function $g(a_3)$, the lower bound of $\delta(a_3)$ can be calculated using (3) for each $a_3$ value and the results presented on a mass fraction ternary diagram (Figure 3). From the stability zone in Figure 3 (solid shading/blue), it can be deduced that all systems inside this (solid shading/blue) region are stable with respect to dissociation and therefore contain at least one bound state. The stability zone saturates the sides of the ternary diagram at $a_3 = 0.8292 \pm 0.0001$, corresponding to $(m_1 = \infty, m_2 = 4.854 \pm 0.003, m_3 = 1)$, and the lower limit of the stability band at $a_3 = 0$ corresponds to a mass ratio $m_1/m_2 = 1.111 \pm 0.001$, i.e., $(m_1 = 1.111, m_2 = 1, m_3 = \infty)$. However, because $\delta(a_3)$ is a lower bound, the stability region may be larger. For example, the system $d^+ t^+ p^-$, consisting of a deuteron, triton, and anti-proton lies just outside the calculated stability zone, however this species is predicted to have a weakly bound ground state.\textsuperscript{34-36} Additionally, literature values indicate that the minimum mass required to bind a “positron” to a hydrogen atom with an infinite nuclear mass is between 1.51 $m_e$,\textsuperscript{15} and 2.20 $m_e$,\textsuperscript{14} whereas our results suggest that a mass of 4.85 $m_e$ would be required. The inaccuracy in the present result is due to underestimation of the width of the stability band. The lower limit of the stability band (3) is derived by rewriting the Hamiltonian as a sum of symmetric terms (symmetric under $1 \leftrightarrow 2$ exchange) and anti-symmetric terms, and then applying the variational principle to this Hamiltonian using the symmetric ground state of the symmetric Hamiltonian as a trial wave function.\textsuperscript{13,22}

This underestimate would indicate that the anti-symmetric (symmetry-breaking) terms are not small.\textsuperscript{37} Clearly, a more accurate value could be obtained by solving the Schrödinger equation for three unequal mass particles directly.\textsuperscript{38} Further work will involve using a method to predict a more precise bound based on determining the value of the third particle mass that corresponds to the critical binding energy, i.e., when $E_0 = E_{th}$. Particularly interesting is the mass ratio of the system which corresponds to the minimum in the function $g(a_3)$ as $Ps^- (m_1 = m_2 = m_3 = 1)$ actually possesses the smallest value of $E_0 - E_{th}$ and thus has the smallest magnitude of energy gain due to the presence of a third particle. However, it does not possess the least fractional gain as defined by $g$; nor is $g(a_3)$ minimal for $a_3 = 0$ which would correspond to $\infty H^-$.\textsuperscript{22} This determination is, to our knowledge, the most accurate to

![FIG. 2. (a) Plot of $g$ against $a_3$ for a range of symmetric systems, (b) the function $g(a_3)$ (red line) compared with the raw data of $g$ versus $a_3$ (green crosses).](image)

![FIG. 3. The stability domain (solid shading/blue) derived from the binding energies of the systems along the symmetry axis.](image)
date. Moreover, a recent study into the emergence of molecular structure in Coulombic three-particle systems considered the distribution of the identical particles in the ground state and concluded that a node in the particle density at the centre of mass first appears when $0.4 < m_1/m_3 < 0.8$. It is suggested that such a transition in density distribution could determine the crossover point between molecular and atomic behaviour. The results presented here, suggest that this cross-over point causes a destabilisation and thus corresponds to the system with the least fractional gain in binding energy by association with a third particle.

IV. CONCLUSIONS

In this paper, we have unified the treatment of “atomic” and “molecular” type systems by solving the Schrödinger equation for three-particle systems in translation-free internal coordinates using a wave function expanded in a triple orthogonal set of Laguerre functions with two nonlinear parameters. A range of symmetric unit-charge systems have been calculated to high accuracy and used to predict the width of the stability band in terms of the fractional additional binding $g$ as a function of the reciprocal mass of the uniquely charged particle, $a_3$, using the method of Martin et al. A functional form of $g(a_3)$ is obtained by fitting to these data and is used to determine the minimum value of $g(a_3)$, the point of least relative excess binding due to a third particle. The minimum is estimated to occur at $m_1/m_3 = 0.491$ which corresponds to $(m_1 = m_2 = 1, m_3 = 2.04)$. Mátýus et al. discuss the emergence of molecular structure in three-particle systems in terms of the density at the centre of mass and calculate that the transition takes place within the interval $0.4 < m_1/m_3 < 0.8$; the results presented here indicate that the transition from atomic-like to molecular-like behaviour occurs when the system has the least energetic gain by association with a third particle.

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